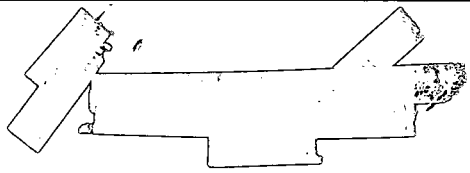

FINAL REPORT

PROJECT HR-116 OF THE IOWA HIGHWAY RESEARCH BOARD
IOWA STATE HIGHWAY COMMISSION

RELATIONSHIP OF CARBONATE AGGREGATES TO CONCRETE AGING

by

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FINAL REPORT OF HR-116

RELATIONSHIP OF CARBONATE AGGREGATES TO CONCRETE AGING

INTRODUCTION

Problem and Objectives

HR-116 is concerned with the relationship of carbonate aggregate to aging of highway concrete. The ultimate purpose of the research is to provide the Materials Department with better criteria for selection of carbonate aggregates for use in highway concrete. The research stems from the problem in Iowa which relates durability of highway concrete to use of certain aggregates. Service records of certain highways have shown that concrete deterioration is related to the source of coarse carbonate aggregate. Research on this problem in projects HR-15 and HR-86 helped define three broad areas of the problem in more detail:

1. The problem of evaluation of rocks which pass current specifications but have poor service records
2. The basic problem of how rocks contribute to distress in concrete
3. The problem of how concrete ages or weathers.

All three are closely interrelated since the evaluation of potential behavior of an aggregate requires an understanding of how rocks contribute to concrete durability. This in turn requires that we understand how coarse aggregate,

fine aggregate and cement interact in concrete as it changes with time. It is in this last area where we lack most knowledge. HR-86 initiated the first research in this area which was continued in HR-116.

The main objective of HR-116 is to determine what changes occur with time and their effect on concrete in terms of:

1. Changes which occur in the matrix
2. Changes which occur in the aggregate

Status of Research

In order to accomplish the above objectives, the proposed areas of investigation for the proposal were:

1. Petrographic studies similar to the Otis type of HR-86 on another series of highway concretes. This study will relate the lithology of aggregates in concrete cores to lithologies in the quarries and to the age and overall condition of the cores.

2. Petrographic and chemical studies will be made in which the concrete under investigation is cored systematically at regular intervals from sound through the deteriorated areas. This type of study would be done on various ages of concrete. The relationship of stress to concrete deterioration, as well

as characterization of the aggregate bond surface and aggregate texture in terms of volume to surface ratios, would be part of this area of research.

3. Chemical and physical study of additional cores of concrete taken from the center of slabs which have good service records and have intermediate ages between 10 and 20 years.

In item (1) it was thought that the Otis type study could be applied to the Argentine aggregate. This was not done at the request of the ISHC. Instead a more thorough study of the Otis lithologies in the quarry as they occur in concrete cores of different ages was made as part of Mr. Elwell's Masters thesis studies. A summary of this study is included as part of this report.

Item (2) concerning the systematic petrographic and chemical studies of cores taken gradationally from sound to deteriorated zone of highway concrete have been called "Fence" studies by us and will be referred to as such from now on. A good start has been made in this area which has produced considerable new data and insight into the problem. The locations and types of concrete and related aggregate used for this study are given in Table I.

Item (3) concerns taking additional cores from the center of slabs for additional data. After consultation with ISHC the program of sampling was restricted to concretes made from Otis and Alden aggregates which were cored in 1966. In all cases the cores were taken in the center of slabs as near

TABLE I

HR-116 PETROGRAPHIC FENCE SAMPLING PROGRAM

FOR DETERIORATED ZONES

CODE	STATION	FEATURE	NUMBER OF CORES
CD-66-58-150	43 + 80	Joint	3
CD-66-52-1	110 + 50	Joint	4
CD-66-51-W	———	Joint	1
CD-66-48-84	161 + 15	Crack	1
CD-66-48-84	161 + 75	Crack	2
CD-66-4800	———	Joint	2
CD-66-48--	———	Crack	1
CD-66-46-1	840 + 65	Contraction Joint	2
CD-66-46-1	840 + 30	Expansion Joint	2
CD-66-41-1	666	Crack	1
CD-66-41-1	665 + 4	Expansion Joint	3
CD-66-38-38	208 + 20	Contraction Joint	2

TABLE II

CONCRETE SAMPLING* PROGRAM HR116

OTIS AGGREGATE CONCRETE

CODE**	STATION	LOCATION
CD-66-61-150	213	HW 150 from HW 151 to old HW 30
CD-66-58-150	59	Relocation HW 150 to HW 151
CD-66-57-W	16	HW W east of Williamsburg
CD-66-56-218	250 + 75	HW 218 from SE¼ 21-8-7 to HW 84
CD-66-52-1	227 + 80	HW 1 north of Mr. Vernon
CD-66-51-W		HW W east of Williamsburg
CD-66-50-64	43	HW 64 and HW 151 in Cedar Rapids
CD-66-48-84	161 + 10	Airport road near HW 218
CD-66-48-151	43	Inside lane on HW 151 in Cedar Rapids
CD-66-48-3	204	HW 3 south east of Edgewood
CD-66-48--		Old HW 30 near Marshalltown
CD-66-46-1	840	HW 1 near Mt. Vernon
CD-66-41-1	666	HW 1 north at Solon

ALDEN AGGREGATE CONCRETE

A-66-65-65	12	HW 65 north of Iowa falls -- north of HW 20
A-66-51-383	22	HW 383 west of Randall
A-66-51-6	1923 + 75	HW 51 east of Newton
A-66-50-14	765 + 80	HW 50 south of Laurel
A-66-41-14	37	HW 14 north of Parkersburg
A-66-36-60	115	HW 60 west of Webster City
A-66-29--	517	Old HW 30 east of Nevada

*The sample consists of seven (7) cores taken at each location

**Explanation of code: Letters represent aggregate; first set of digists is year cored; second set of digits is year paved; last set of digits is highway number.

as possible to the sites which were cored in 1963 for HR-86. In addition it was possible to find some highways built at critical times which removed the datum gaps in the HR-86 program. Table II gives a complete list of cores taken. Seven cores were taken at each sample site. Three were retained by us, three by the ISHC, and one was kept in reserve. The ISHC as it did for HR-86 conducted compressive strength tests on the cores. In addition to that a study of the air content on all cores retained by the ISHC was made in order to determine the effectiveness of air entrainment and the degree of water saturation in the air entrained pores of the concrete. These data provided relationships between plastic air content, normally measured air content, and effective air content in the as-received cores to compressive strength data. This study will be discussed later in the report.

The three items discussed above have served as the main areas of endeavor for HR-116. Before commencing the detailed chemical analyses on the center of slab and fence cores intensive preparatory petrographic and chemical studies were made to determine what procedures and techniques should be applied to provide the maximum amount of data. These preliminary studies consumed considerable time. A thorough review of all data in HR-86 was made in which the chemical data was reworked. This was done to provide a better basis for evaluating old data and setting the direction our new sampling and analytical techniques should follow. These data formed the bulk of an unofficial presentation at the 1966 HRB meeting in Washington, D.C., entitled "Aspects of Highway Concrete Aging in Iowa". Copies of the paper are submitted with this report and a summary of it will be presented later. As a result of this paper

considerable time was spent in working out new chemical techniques of partitioning silica and calcium present in the matrix. This technique now provides us with a means of following the changes which occur in the matrix calcium silicate hydrates.

Petrographic studies of individual pieces of broken concrete and cores taken at the sites where cores were taken for the fence study led to the development of several new techniques and revisions in our analytical methods. Staining techniques and use of acetate peels on sawed sections indicated that the surface of cores, fracture surfaces with their unique coating or films, rim zones, and distribution of ferrous and ferric iron in concrete were critical areas for further study. They also emphasize the need for ferrous/ferric ratios and the silica and calcium partitioning techniques be applied to study vertical changes at the top and 1/4-inch depth in addition to the 1, 3, and 5 inch layers in all the cores taken. The development of these new techniques and recognition of new areas of investigation from an important part of the research accomplished to date.

These studies have provided us with better means of studying the cores to yield more meaningful data. Although they have considerably increased the work and time required to obtain such data, the availability of better means of investigating aggregates and concretes give rise to methods which can be applied in future investigations of aggregate and concrete behavior.

Nature of Report

Following the introduction this report will summarize all the significant work accomplished as part of HR-116. The subject matter will follow a historical approach in which the subject matter will be presented essentially in the order of which it was obtained. The report will be organized according to the following subject areas:

Evaluation of HR-86 Chemical Data

Behavior of Otis Aggregate in Highway Concretes

Phase Changes of Cement Silicates During Aging

Moisture, Air Content, and Strength Studies

Preliminary Investigations for HR-116

Petrographic Study

Chemical Changes with Depth and in Center of Cores

The summary and conclusions of the above subject areas will be presented at the end of the report along with a discussion for future research.

Theses and Publications

In the course of the investigations, the following thesis was submitted during the course of HR-116:

1966 -- James Halsey Elwell

Behavior of Carbonate Aggregate from the Otis Member of the Wapsipinicon Formation in Highway Concretes of Various Ages.

An abstract of a paper to be presented at the meeting of the Geological Society of America in November of 1967 has been prepared:

1967 -- Elwell, James H., Simon, David E. and Lemish, John
Carbonate Aggregate Reaction Rim Behavior in Highway Concretes.

An off-the-record paper was presented at the Forty-fifth Annual Meeting of the Highway Research Board in January of 1966.

1966 -- Elwell, James H., Moore, W. F. and Lemish, John
Aspects of Highway Concrete Aging in Iowa.

Personnel

The project has been under the direction of Dr. John Lemish and was conducted in the laboratories of the Department of Earth Science at Iowa State University. The work was accomplished through the efforts of the following graduate student research assistants: Mr. James H. Elwell and David Simon. Mr. Steven Zimmerman performed chemical analyses on an hourly basis. Mr. Gary Kuberski, Paul Mack and Miss Helene Wing prepared samples for chemical analysis.

Acknowledgements

The cooperation of the Iowa State Highway Commission Materials Department is acknowledged. Mr. Tom E. McElherne, head of the Materials Department, is

thanked for his cooperation. Mr. Ted Welp, Senior Geologist for the Materials Department helped with selection of highways for coring and spent considerable time and effort in setting up the coring program. Mr. Kenneth Isenberger, Materials Geologist, helped with the coring program.

EVALUATION OF HR-86 CHEMICAL DATA

Before commencing the coring program and setting up analytical procedures a review of the HR-86 chemical data obtained from the center of slab cores was made to provide as much information as possible which could be applied to HR-116. New and additional data were obtained to allow us to partition the calcium in the matrix. This was done after the chemical data had been written for the unofficial HRB presentation on our aging studies which is submitted as a supplement to this report. In order to avoid duplication a brief summary which takes into account the recent calcium partitioning data is included as part of this report. The section on chemical data in the HRB report was therefore removed. A major result of our evaluation of the HR-86 data which contributed most to HR-116 was the recognition that changes were dependent on and must be considered in terms of the sources of cement and aggregate before any conclusions can be drawn.

In HR-86 the samples were studied at the 1", 3", and 5" depths as shown in figure 1. The matrix consisting of hydrated cement paste and fine aggregate was tediously separated by hand from the coarse carbonate aggregate. Chemical analyses were made of both the matrix and coarse aggregates. The matrix was analyzed for S_1O_2, CaO, MgO, Al_2O_3, Fe_2O_3, Na_2O, K_2O, SO_3, CO_2, and H_2O. In HR-86 the matrix data was of main interest and the weight percent analytical data was plotted across the log of time to detect any bulk chemical changes. Some general changes in bound water, CO_2, O, and MgO were noted as was the fact that non-air entrained concretes had a slower rate

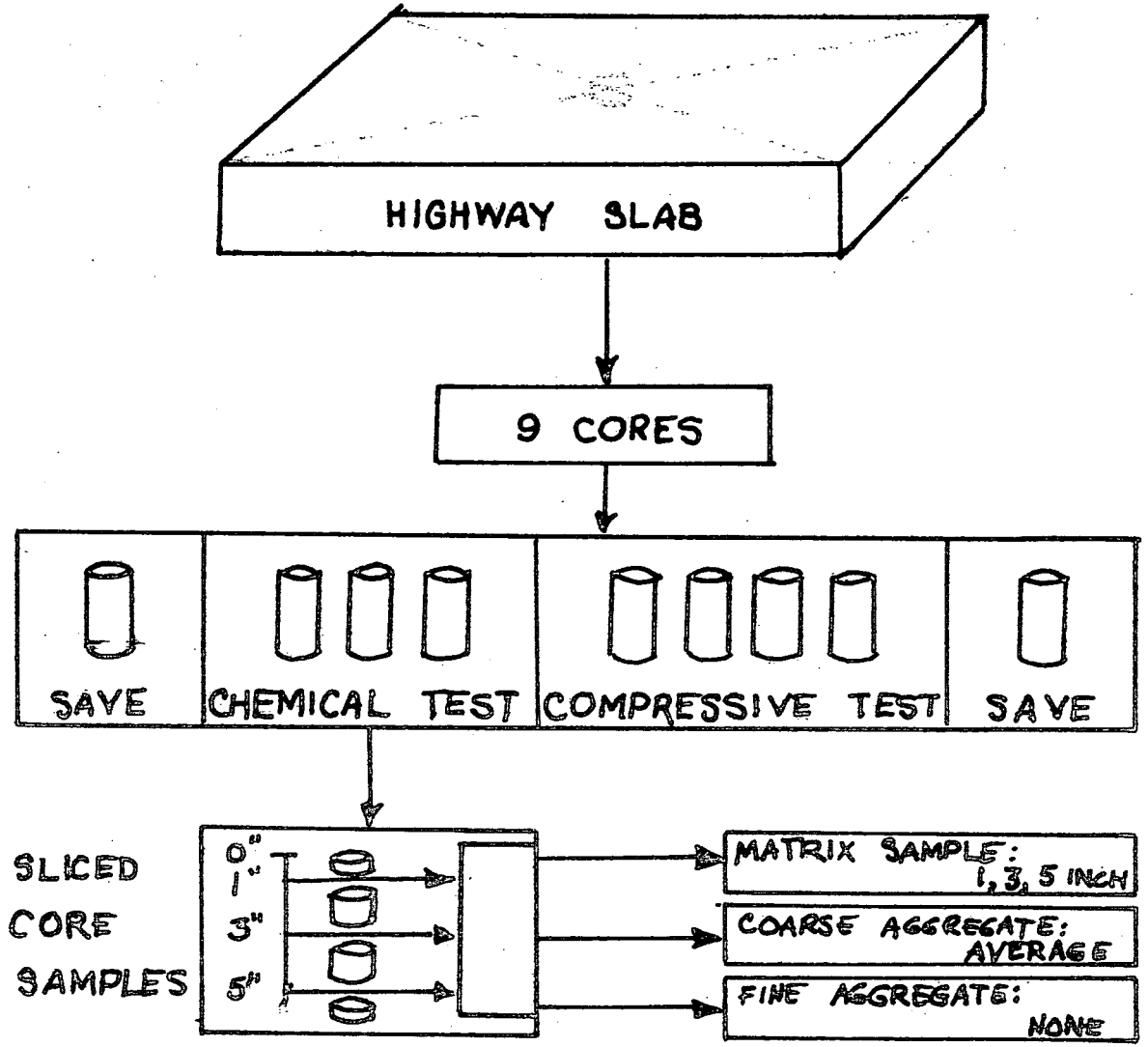


Figure 1 Primary sampling.

of chemical change than the air entrained concretes. These data are presented in Table III.

A major problem encountered in HR-86 was the fact that the matrix fraction when ground prior to analysis contained both fine aggregate fraction as well as the material derived from cement. Since our primary interest was in changes occurring with time in the cementing materials, it became apparent during the course of our evaluation that the bulk chemical data had to be evaluated on a silica free basis. (Recognition of this fact also led to later study during our preparatory investigations to develop a technique of separating out fine aggregate from cementing material prior to analysis which led to development of the silica partitioning technique and a means of determining the $Ca(OH)_2$ content). Unless the fine aggregate silica is removed, the analytical data represent the properties of concrete matrix but not the cement portion of the system unless the effect of the fine aggregate fracture can be removed by recalculation. The recalculated samples would then be an estimate of the composition of the cement fraction. Since no samples of the original cement were available, it was necessary to assume that cement composition from a particular source would be relatively constant and changes in concentration of the cement fraction would be attributed to aging rather than variation in cement manufacturing.

A method for recalculating the matrix analyses to a basis dependent on the material in the cement fraction was worked out and was defined as a "cement oxide" basis. The few steps are shown in figure 2 and data are presented on Table III. The method partitions the data into cement oxides (CaO, MgO, Al_2O_3, Fe_2O_3, Na_2O, and SO_3) and a fraction containing CO_2,H_2O, and SiO_2.

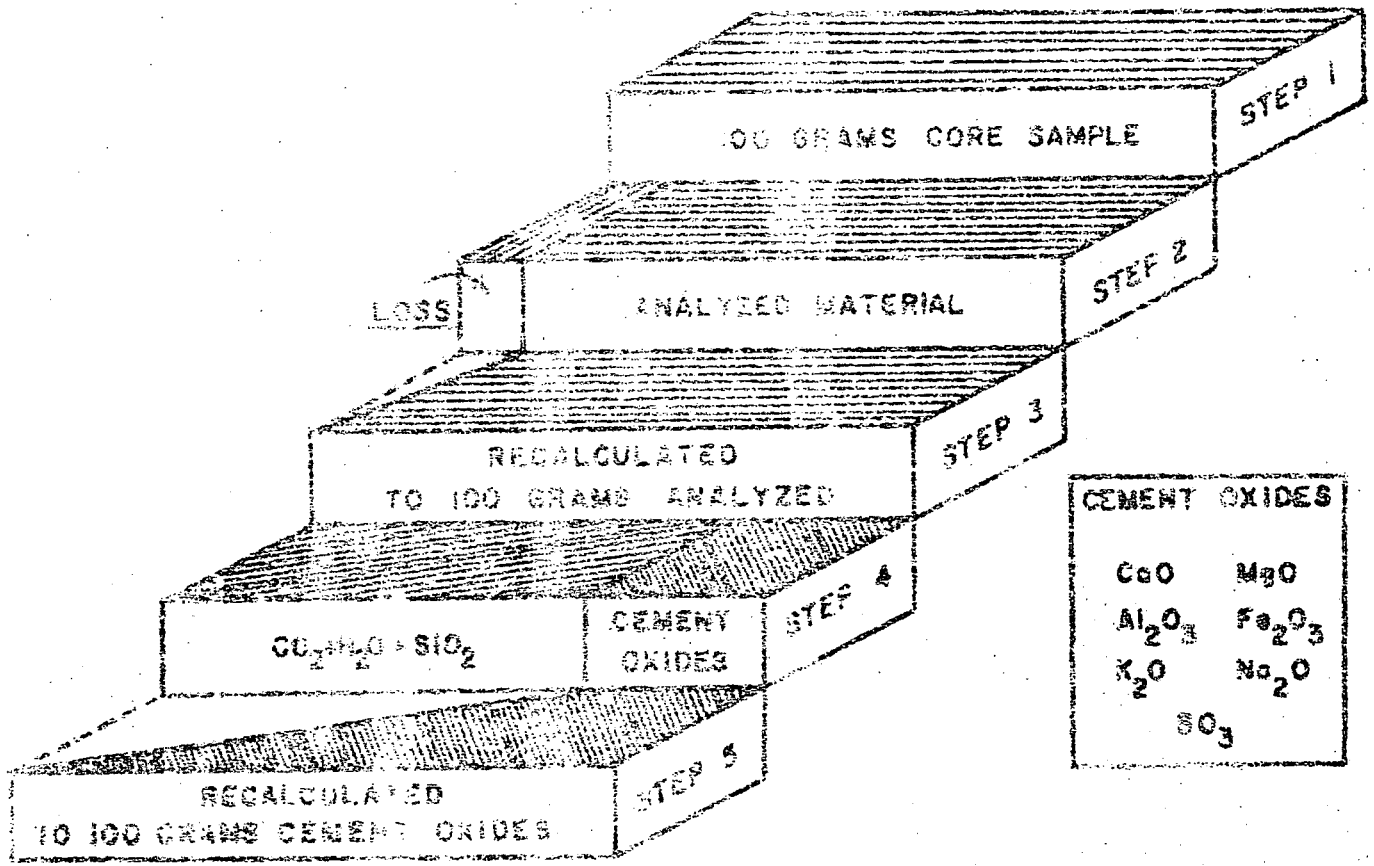


Figure 2 Schematic diagram explaining the calculation methods used to establish the cement oxide basis for defining matrix compositional changes.

Table III CHEMICAL ANALYSIS DATA OF MATRIX MATERIAL TAKEN FROM 1963 CORES, REPORTED ON TOTAL WEIGHT PERCENT BASIS. (VALUES SHOWN ARE AVERAGE OF DATA OBTAINED ON SAMPLES AT 1, 3, AND 5 INCH DEPTH).

Weight % Core #	SiO_2	Total CaO	MgO	Al_2O_3	Total Fe_2O_3	Na_2O	K_2O	SO_3	CO_2	% Free CaO*	% FeO	Wt.Loss @ 950°	Total %
Cd-61	57.46	18.30	2.53	1.70	1.35	0.12	0.13	1.47	1.84	5.33	0.15	9.97	93.03
Cd-58	58.88	20.39	2.13	1.60	1.36	0.07	0.08	1.44	2.33	4.51	0.07	10.60	96.55
Cd-56	53.36	18.91	3.47	1.45	1.70	0.07	0.11	1.67	6.57	1.65	0.19	13.13	93.87
Cd-52	55.08	18.10	3.67	1.80	1.25	0.07	0.11	1.31	3.89	4.35	0.15	11.02	92.41
Cd-46	54.43	18.56	3.84	1.70	1.52	0.09	0.10	1.01	5.02	3.18	0.15	12.36	93.61
Cd-41	54.51	19.61	1.85	1.06	1.89	0.09	0.11	1.41	4.87	1.62	0.19	11.80	92.33
Cd-38	49.60	25.13	3.87	1.47	1.61	0.09	0.09	1.09	8.77	3.28	0.03	15.51	98.46
Ia-27	58.09	19.10	1.77	2.12	1.46	0.08	0.09	1.60	2.20	-	-	10.77	95.08
Ia-6	53.74	19.00	1.57	1.86	2.25	0.14	0.17	1.52	3.43	-	-	11.36	91.61
Ad-14	54.85	16.59	2.31	1.25	3.00	0.11	0.17	1.20	3.77	1.40	0.76	10.43	89.91
Ad-60	48.08	28.10	4.11	1.93	1.89	0.12	0.15	0.86	6.77	3.06	0.02	14.13	99.37
Ad-57	53.17	23.65	2.87	2.02	1.90	0.12	0.14	0.99	3.55	3.45	0.09	12.19	97.05
Du-27	58.20	19.62	2.92	1.68	1.72	0.08	0.12	1.15	2.83	-	-	9.13	94.62
Du-32	53.84	20.38	3.96	1.87	2.32	0.14	0.17	0.92	2.07	-	-	10.33	93.93
Du-20	55.80	20.47	3.49	2.06	1.98	0.09	0.21	1.07	3.65	-	-	10.91	96.08
Du-26	56.47	19.95	3.41	1.77	2.24	0.07	0.16	1.03	3.43	-	-	10.52	95.62
Dc-28	42.06	23.39	3.84	1.90	1.68	0.11	0.20	2.05	7.49	-	-	15.93	88.44
E1-40	57.12	17.34	1.34	1.90	1.81	0.08	0.10	0.25	3.68	-	-	10.58	88.04

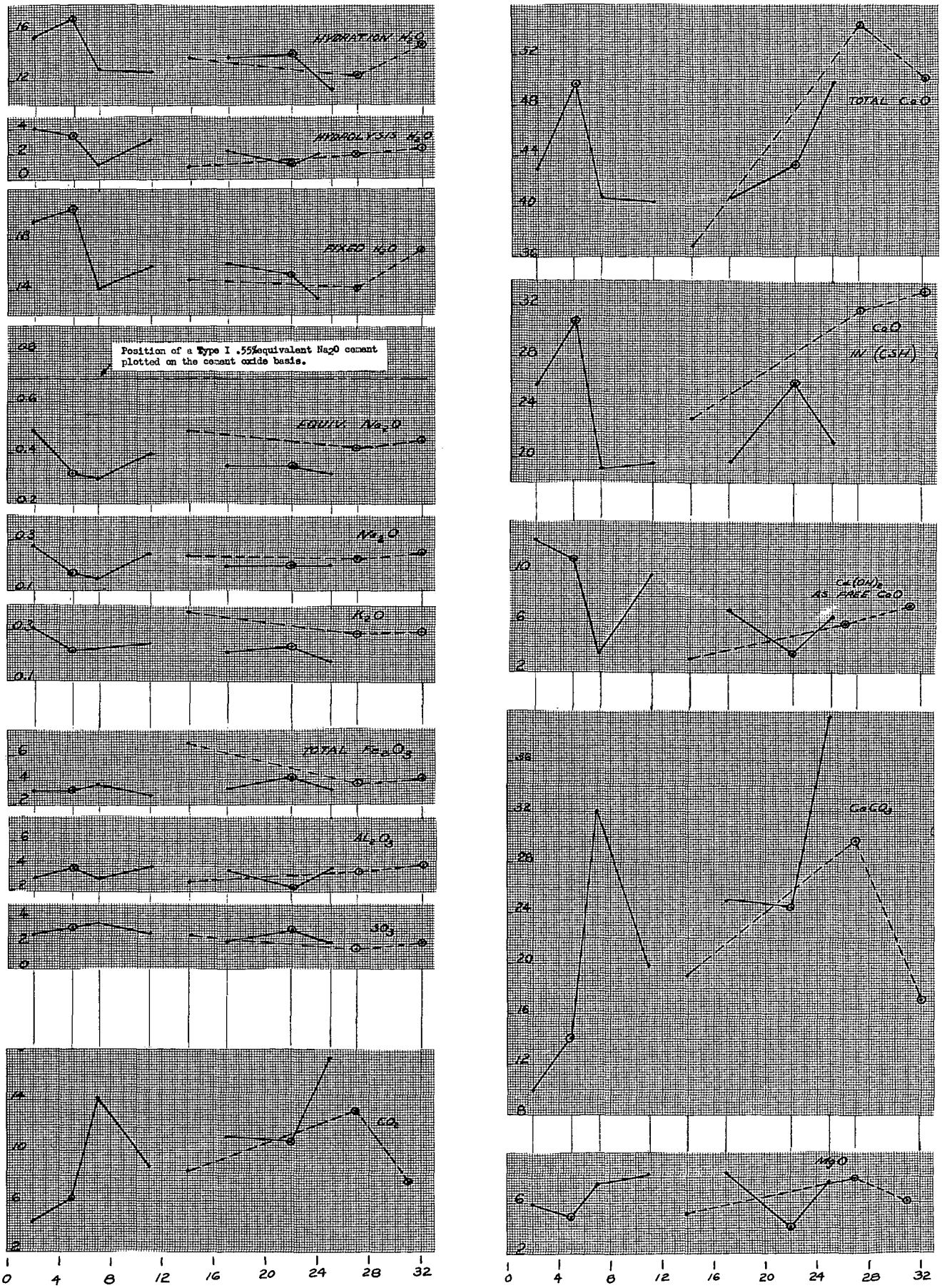
* $Ca(OH)_2$ reported as CaO

The cement oxide portion was then recalculated to a basis of 100 grams of cement oxides. The weight of CO_2 and water associated with this new basis was also calculated. As a result of this approach it was possible to compare in a meaningful way the changes which occur in the cement fraction of the matrix with time.

Table IV presents the additional data obtained as part of HR-116 on the 1963 cores which allows us to evaluate the amount of calcium silicate hydrate (CSH) compounds in the cement fraction of the matrix. This was possible because of the calcium and silica partitioning studies mentioned in the introduction. As a result of these additional data, a series of graphs using our cement oxide basis are presented in figure 3 showing the chemical changes in concretes with time. These data represent average values and are confined to Otis and Alden aggregate concretes. The data are also plotted with regard to source of amount and to show the air entrainment break. The data points older than 1952 represent non air-entrained concrete. Concretes younger than 1952 are air-entrained. This division is essential because they are different concrete systems and must be treated separately. The importance of this break is especially well demonstrated on the total CaO and $Ca(OH)_2$ cores.

The alkali behavior with time shows that all the concretes lose alkali to an equilibrium concentration soon after they are poured. These data show that mobile ions such as K_2O and Na_2O are rapidly removed from the concrete system (later data show much of the alkali is concentrated at the surface) to an equilibrium concentration.

Al_2O_3 remains at a fairly constant concentration as does Fe_2O_3. The Fe_2O_3 in non air-entrained Alden appears to have decreased with time.



— OTIS AGGREGATE, ---ALDEN AGGREGATE, • DEWEY CEMENT, ⊙ PENN DIXIE CEMENT

FIGURE 3. VARIATION OF THE CHEMICAL COMPOSITION OF THE MATRIX COMPUTED ON A SILICA FREE CEMENT OXIDE BASISWITH TIME. DATA REPRESENT AVERAGES OF THE 1,3, and 5 INCH DEPTHS.

Table IV CHEMICAL ANALYSIS DATA OF MATRIX MATERIAL TAKEN FROM 1962 CORES, REPORTED ON SOLUBLE[1] WEIGHT PERCENT BASIS. (VALUES SHOWN ARE AVERAGE OF DATA OBTAINED AT 1, 3, AND 5 INCH DEPTH).

	SiO_2*	Total CaO	MgO	Total Fe_2O_3	Al_2O_3	Na_2O	K_2O	Wt.Loss @950°C	SO_3	Fixed H_2O ¥	Free CaO**	CO_2	FeO	CaO# in(CSH)	H_2O¢ Hydration
CD-61	135.03	43.01	5.95	3.17	3.13	0.28	0.31	23.83	2.75	19.41	12.53	4.42	0.35	24.84	15.39
CD-58	143.10	49.72	4.98	3.21	3.84	0.17	0.22	26.12	3.33	20.44	10.96	6.22	0.17	30.84	16.91
CD-56	114.83	40.70	7.46	3.66	3.12	0.15	0.23	28.25	3.59	14.10	3.55	14.15	0.41	19.11	12.96
CD-52	122.82	40.36	8.18	2.79	4.01	0.25	0.25	24.60	2.92	15.88	9.70	8.70	0.33	19.58	12.76
CD-46	119.20	40.65	8.41	3.33	3.72	0.20	0.22	27.09	2.21	16.07	6.96	11.02	0.33	19.67	13.84
CD-41	120.03	43.19	4.07	4.16	2.33	0.20	0.24	25.89	3.10	15.18	3.56	10.74	0.42	25.96	14.04
CD-38	98.21	49.76	7.66	3.19	2.91	0.20	0.18	30.69	2.14	13.33	6.49	17.34	0.06	21.15	11.25
A-14	121.87	36.87	5.15	6.68	2.78	0.24	0.38	23.18	2.66	14.81	3.11	8.37	1.69	23.09	13.81
A-60	92.81	54.25	7.93	3.65	3.65	0.23	0.29	27.27	1.66	14.19	5.91	13.07	0.04	31.69	12.29
A-57	114.14	50.14	6.08	4.03	4.09	0.25	0.30	24.66	2.10	17.13	7.31	7.53	0.19	33.22	14.78

* SiO_2= Percent associated with 100grams of soluble sample.

** Free CaO = $Ca(OH)_2$ reported as CaO

¥ Fixed Water = (% Wt. Loss @ 950° C) - (% CO_2)

CaO in (CSH Compounds) = (Total CaO) - (Free CaO) - (CaO in $CaCO_3$)

¢ H_2O of Hydration = (Fixed H_2O) - Water of Hydrolysis (H_2O assoc. with Free CaO)

1 All material that is soluble in HCl = (Total wt.) - (SiO_2)
(All SiO_2 rendered insoluble by dehydration)

MgO shows a gradual increase with time in the air-entrained Otis aggregate concrete. This may reflect the addition of MgO from the coarse aggregate as a result of the alkali aggregate reaction.

The SO_3 content remains stable with time.

Although total CaO increases with time in both Alden and Otis aggregate concretes, the variation in CaO when partitioned as CaO in CSH and $Ca(OH)_2$ behave differently. The Otis aggregate concretes are losing CaO in CSH and $Ca(OH)_2$ compounds. The Alden aggregate concretes steadily show an increase of CaO in CSH and $Ca(OH)_2$ compounds indicating that the CSH materials are stable and are still hydrating after 30 years of service. The fixed water, and hydrolysis and hydration H_2O curves reflect these changes.

The greatest contrast in the performance of both concretes is seen in the CO_2 and $CaCO_3$ curves. Otis aggregate concretes show an increase in these components - whereas the Alden concrete do not.

From these data it is evident that Otis aggregate concretes are carbonating and losing their CSH compounds with time.

In summary, the data show that alkali content decreases to an equilibrium concentration soon after paving. Al_2O_3, Fe_2O_3, and SO_3 show little change. The greatest differences in terms of change are in the calcium compounds among which the CaO, CO_2 and various waters are partitioned. The Otis aggregate concretes show an increase in calcium carbonate and loss of $Ca(OH)_2$ and CSH compounds with time. Alden aggregate concretes show a gradual increase in $Ca(OH)_2$ and CSH compounds with time which coincides with its excellent service record. These data show the basic ways the concretes change with time.

BEHAVIOR OF OTIS AGGREGATE IN HIGHWAY CONCRETE

Introduction

The research on this subject resulted in a Masters thesis written by James H. Elwell. Copies of the thesis are submitted as part of the final report and a brief summary of investigation and its conclusions will be presented.

Summary

The unique aspect of the research in this area was the attempt to relate individual pieces of coarse aggregate observed in concrete to the exact ledges in the quarry from which they came. This was done at several levels of investigation (macroscopic hand specimens and microscopic thin and opaque sections) so that the relationship of aggregate to quarry ledge was accomplished. Since Otis aggregate concretes show deterioration within 14 to 17 years it was suspected that this was caused by dilution of good performance aggregate by poor performance material undetectable by present physical or chemical facts.

Observations made on the bending strength of the matrix-coarse aggregate bond were related to this study and have been described in the thesis and the paper on aging. The bending strength studies separated the lithologic types into stronger and weaker classes (Table V). The weak class fails only

TABLE V CHANGE IN FIRST FAILURE LOCATION WITH TIME.

Curve / Load	A	R_1	BZ	R_2	M
1961			23, 22, [9], [11], [15], 10, 20, [13]		
1968	[15], [13]	[9], [11]	23, 22, 19, 18, 10		17, 20
1958	[21], [13]		[21], 22, 23, 18, [15], 10, [11], 16		20
1952		[11]	[21], [9], [15], [13], 19		17, 22, 23, 10, 16
1946	[21], [13], [15], [21]	[11]	16		17, 22, 23, 19, 10
1941	[21], [15], [11]		16, [13]		17, 23, 19, 18, 20, 10
1938	[21], [15]	[15]	23, 22, 16	17, 18	20

[ ] Indicates lithologies weaker than matrix

in the bond zone or within the inner rim of the aggregate; the stronger class fails in only the bond zone and matrix. Although initially both classes fail in the bond zone, after a period of time each class progressively demonstrates its unique zone of failure which characterizes the weak and strong lithologies. These lithologic and breaking studies made it possible to establish the differences between various lithologies which constitute Otis aggregate.

Following this a petrographic study of the various lithologies of Otis aggregate on cores of different ages from the center of slabs obtained during HR-86 was made to detect how various types of Otis lithologies responded to the same environment.

After the separation of lithologic types into classes and the progressive changes characteristic of each type, petrographic study of the entire core-matrix and coarse aggregate was undertaken and the aspects investigated were air entrainment, rim growth, recrystallization, matrix-fine aggregate interaction, highway surface behavior, and concrete fracture behavior.

Air entrained concretes were associated with increased leaching of the matrix and aggregate materials and an increase in the rate of chemical reaction. Non-air entrained concretes showed less evidence of leaching of matrix and aggregate so that their color closely approached that observed in the quarry.

The negative type rims were found to form early in the life of the concrete (28 day test cylinders). The rims were recognized by color zonation (lighter at outer edge). In older concrete the entire particle of the rim forming lithologies were converted into rims. Rim coloration was considered the result of differential leaching of iron impurities from aggregate; some

of the leached iron formed a dark outer rim in the matrix.

Recrystallization zones and strained areas were found in older concretes associated with the rim zones and outer boundary of the coarse aggregate.

Matrix-fine aggregate interaction was studied and in air entrained concrete voids within the matrix were partially filled with carbonate material leached from the coarse aggregate. Most of the voids were open or filled with a brown gel and a crack network developed between the void and surrounding fine aggregate particles. Non-air entrained concrete showed less leaching, pore filling, brown gel and no crack network in young concrete; progressive filling of pores and crack development in older cores. Brown gel was found in the matrix and in grain boundaries of quartz and feldspar. Cracks between the fine aggregate particles and voids were usually associated with gel pockets and secondary minerals.

Study of highway surfaces indicated that with time the fine aggregate is lost and the surface roughness is due to differential behavior of the coarse aggregate. Loosening of the bond between concrete material and fine aggregate was associated with presence of brown gel on surfaces and in the matrix. Movement of the gel could be traced from the exposed coarse aggregate into the matrix and fine aggregate.

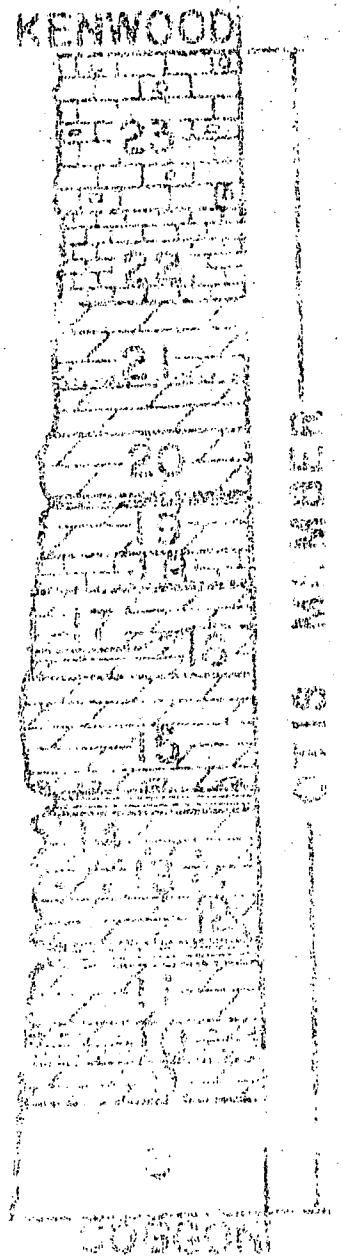
Investigations were made on the fracture behavior of thin slices of broken concrete. Fracture path was found to be related to interfaces of coarse or fine aggregate particles except where gel or recrystallization had weakened bonding.

Conclusions

The study shows that iron gel derived mostly from pyrite in Otis stone can be related to behavior of the weaker class lithologies recognized. These observations on behavior of iron gel in inner and outer rim zones, interaction with fine aggregates and fracture surfaces clearly indicates that an iron gel-forming reaction was recognized. Concentrations of gel appear to cause trouble both in the process of forming negative rims and causing onion-skin type failure and in the matrix where it is associated with disruption of the fine aggregate-cementing material bond.

The demonstration of methods of recognizing, tracing, and relating coarse aggregates to the source in individual quarry ledges is a valuable contribution to future studies of concrete deterioration. Recognition of "weak" and "strong" lithologies is applicable in other studies. A practical result is recognition that most of weak lithologies occur in the lower half of the quarry (Figure 4). This suggests that further investigation on the potential performance of upper ledges containing "strong" lithologies could be undertaken.

OTIS QUARRY SECTION
SE 1/4, NW 1/4, SEC. 34, T83N, R7W
LYNN COUNTY, IOWA



23	LIMESTONE
22	LIMESTONE
[21]	DOLOMITE
20	DOLOMITE
19	DOLOMITIC LIMESTONE
18	LIMESTONE
17	DOLOMITIC LIMESTONE
16	DOLOMITIC LIMESTONE
[15]	DOLOMITE
14	SHALE
[13]	DOLOMITE
12	SHALEY SEAM
[11]	DOLOMITE
10	DOLOMITE
[9]	DOLOMITE
8	COVERED BY TALUS
[ ]	WEAK LITHOLOGIES

Figure 4 Stratigraphic distribution of weak lithologies.

PHASE CHANGES OF CEMENT SILICATES DURING AGING

Although the overall chemical changes associated with aging of concrete was emphasized in HR-86, an attempt was made to identify the various phases or compounds present in the matrix. The purpose of this was to investigate any systematic changes in matrix compounds which might occur with time. Previous work here and elsewhere has shown that the common phases found in the matrix cementing material consist principally of various calcium silicate hydrates (called CSH compounds by cement chemists), calcium hydroxide, the universally present calcium carbonate, and calcium sulfoaluminate. Previous petrographic studies show that carbonation occurs and therefore changes in the phases were expected at the expense of the main sources of calcium, the hydrated calcium silicate compounds and calcium hydroxide.

X-ray diffraction studies indicated that the above phases were present but it was extremely difficult to determine these phases quantitatively. The severe limitations were caused by difficulty in getting enough matrix material and their weak and broad diffraction lines in x-ray methods. The chemical change was studied by comparison of bulk chemical data obtained by chemical analysis of matrix material which is reported as weight percentage of the oxides and only the net transfer of material was studied. No direct information as to the changes in the structure of the matrix phases was available.

Dr. C. W. Lentz of Dow-Corning Corporation had developed a technique for extracting structures intact from minerals and portland cement and had applied it to show change in laboratory hydrated cements with time. His technique is to leach the matrix material of concrete in acid to which trimethylsilyl (a form of silane) has been added. New organo-silicates are formed when the silane blocks the dissolved species of silicate. These organo-silicates have the same structure as the compound or phase from which they were derived and it is possible for him to determine the percentage of each structural form present.

With this technique he was able to distinguish the ratio of the monomer (SiO_4), dimer (Si_2O_7) and higher polysilicate structures. Lentz applied this technique to laboratory cement and for short time tests found that in time the monomer was converted to the dimer and the dimer was converted to the polysilicate structure. Detection of this change and particularly the rate of change is important since the monomer and dimer structures are thought to form the "glue" in concrete. In particular, toberomorite is associated with the dimer structure. Thus, in practical terms, loss of the dimer structure should be equated with loss of bonding and tensile strength in the concrete. However, since this is a new technique little information is available as to the rate of this structural change in highway concrete systems. For this information, Lentz needed samples of known cement which spanned considerable service life. In our HR-86 cores represented samples.

Because Lentz had the technique and the expensive equipment necessary to detect the structural form, and we had the necessary core samples, a cooperative study was arranged in which we provided the material as a finely ground powder and Lentz in return determined the percentage of each structure present in our samples. Each party would be free to publish the results in the interest of advancing the state of knowledge. This section of the report

deals with the information provided by Lentz which was obtained on our samples. It provides independent verification of the cement source dependence detected in our bulk studies and relates directly with knowledge gained from our cement calcium balance and silica partition data.

Samples provided to Lentz were selected to give us the most information for the fewest samples. Two cements, Penn-Dixie and Dewey, were provided to evaluate the effect of initial cement composition. A good service record aggregate (Alden) and a poor service record aggregate (Otis) were selected to see if the rate of structural change was markedly influenced by the source of the coarse aggregate.

The results furnished by Lentz are presented in Table VI and shown in figure 5. The curves shown were drawn according to the cement classification and the points on the curves are identified as to source of coarse aggregate. The following points are evident from the reported data.

1. The direction of the observed changes namely those in which the monomer is converted to the dimer and the dimer is converted to the polysilicate is related to the passage of time.

2. The separation between curves of the same structural form indicates a difference in the initial proportion of these silicate structures. Rough extrapolation of these data back to zero time would show that the expected value for concrete made from Dewey cement would have a higher ratio of polysilicates to the other forms than that made of Penn-Dixie cement. Dewey source concrete would also have a slightly higher ratio of the dimer than would be expected of the Penn-Dixie source concrete. This is interpreted to indicate that concrete made from Penn-Dixie cement initially has more potential "glue" or binding material.

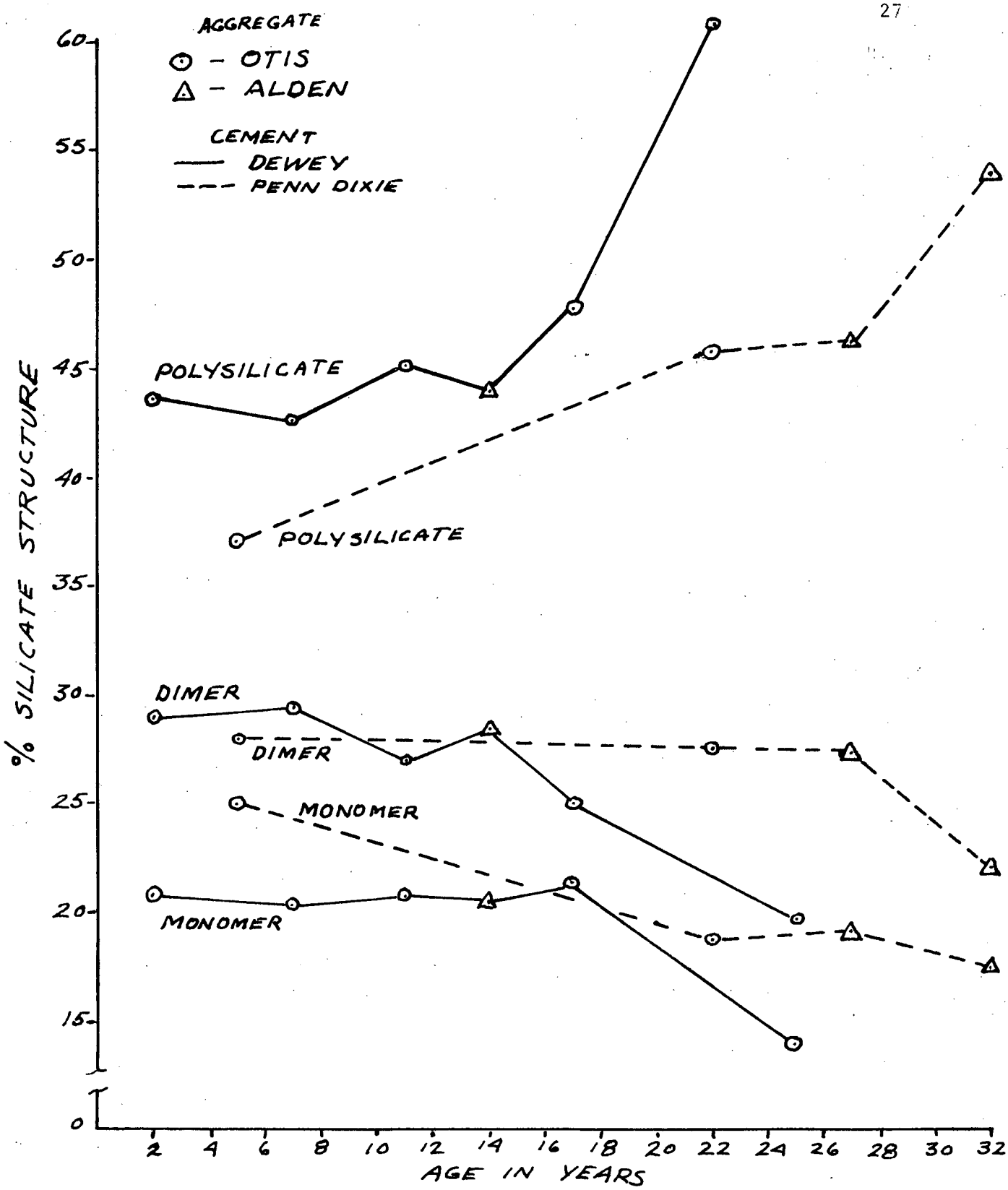


FIGURE 5. THE CHANGE WITH TIME OF SILICATE STRUCTURES PRESENT IN HYDRATED CEMENT PASTE OF THE MATRIX. (DATA FROM 1963 HR 86 CORES).

Table VI: DISTRIBUTION OF SILICATE STRUCTURES IN THE MATRIX OF AGED CONCRETE (AFTER LENTZ)

CODE	AGE	CEMENT	COARSE AGGREGATE	% MONOMER	% DIMER	% POLYMER	TOTAL
CD-61	2	Dewey	Otis	20.8	28.9	43.7	93.4
CD-56	7	Dewey	Otis	20.4	29.4	42.6	92.4
CD-52	11	Dewey	Otis	20.8	26.9	45.2	92.9
AD-14	14	Dewey	Alden	20.5	28.4	44.0	92.9
CD-46	17	Dewey	Otis	21.4	25.0	47.9	94.3
CD-38	25	Dewey	Otis	14.0	19.7	61.1	94.8
CD-58	5	Penn-Dixie	Otis	25.0	28.0	37.1	90.1
CD-41	22	Penn-Dixie	Otis	19.2	27.6	45.8	92.6
AD-60	27	Penn-Dixie	Alden	19.1	27.4	46.4	92.9
AD-57	32	Penn-Dixie	Alden	17.5	22.1	54.3	93.9

3. The average slope of the polysilicate curve for Dewey concrete is increasing more rapidly with time and appears to change with an increasing rate at an earlier age than the Penn-Dixie concrete. This is interpreted to indicate that Dewey cement not only starts with less binding material but loses it at a more rapid rate.

4. As shown in the curves the gross behavior is best explained in terms of changes to an initial ratio of structural forms in the initial cement source. However, the source of the coarse aggregate has a modifying effect on these data. When concretes containing Alden aggregate material are substituted for the expected value estimated from just the Otis aggregate material the difference is always in the direction that would indicate that the loss of binding phases is retarded in the Alden aggregate concrete. Since Alden has a good service record and Otis has a poor service record of highway performance this interaction between the coarse aggregate and the cement dependent properties of the concrete is of interest.

5. Since the monomer appears to pass through the dimer structure before it is converted to polysilicate structures, the higher initial monomer content of the Penn-Dixie cement source may be a clue as to the lower rate of conversion of this concrete to the polysilicate structure.

6. It would appear for these data that Penn-Dixie source cement would produce a more durable concrete than Dewey source cement. If service records of other highways confirm a difference in the behavior between highways constructed using these sources, then these data suggest that information as to the relative abundance of structural forms of silica (alite-belite ratio) in the original cement might serve as an additional basis for cement specifications.

Figure 6 shows the changes in compressive strength for concrete with time coded in the same manner as the Lentz data. Comparison of this curve with the polysilicate curve yields little correlation between these data. It is therefore concluded that the compressive strength is measuring a material property which differs from the structural property of the silicates.

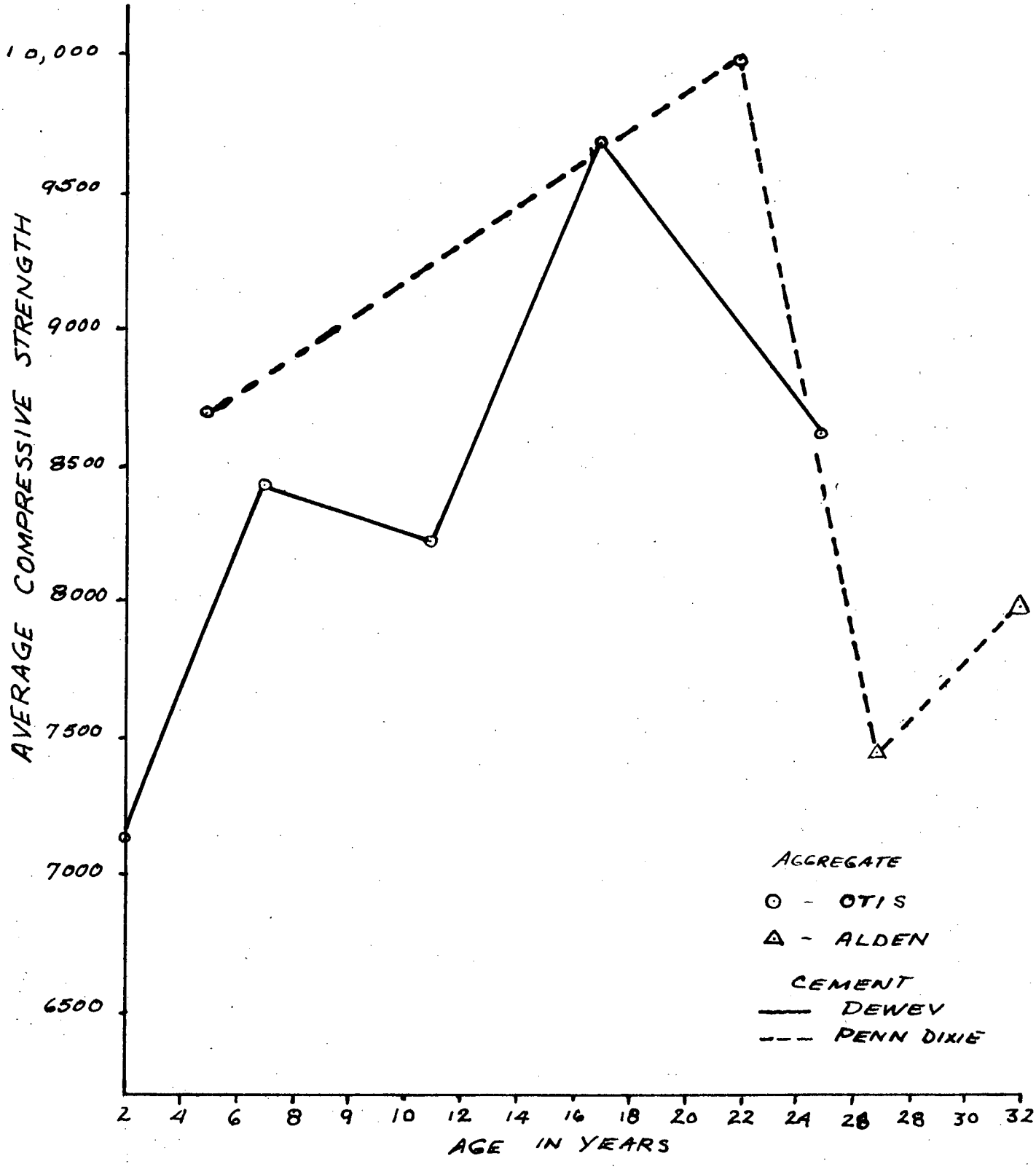


FIGURE 6. CHANGES IN COMPRESSIVE STRENGTH OF CONCRETE WITH TIME.

MOISTURE, AIR CONTENT AND STRENGTH STUDIES

Introduction

Since about 1948 the air content of Iowa highways has been sampled and tested to insure that sufficient air is present to impart freeze thaw resistance to highway concrete. Initial plastic air data represents the air contents introduced into fresh concrete. After the concrete has set the present method of evaluating the air content consists of a standardized test in which water is injected into air entrainment sized voids under specified pressure. The net amount of water injected is reported as percent air.

The standard test requires that cores be dried and then soaked in water to fill larger voids prior to determination of air content. In normal evaluation of highway concrete the core is faced and compressive strength is determined on a particular core before dried weight is obtained prior to air content testing. Air contents obtained in this fashion are used as reproduceable empirical numbers which correlate with freeze and thaw resistance of the highway. Since the water table in Iowa is close to the surface, highways may remain in contact with water a large part of each year. The question of how much water is present in the highway in air entrainment sized voids might bear on effectiveness of air entrainment resistance imparted to reduce freeze and thaw damage. The water we are interested in measuring is that water present in smaller sized voids measured by the water injection technique. This trapped water does not communicate readily with water present in larger voids

so it is assumed that soaking cores for 48 hours or water added to cool the drill bit during coring of the highway does not change the amount of water to be measured because the cores are soaked for 48 hours prior to water injection in the standard air determination in order to fill and remove the effects of the larger voids.

HR-116 Program

The program developed for HR-116 was as follows:

1. To determine if the water content of highways could be measured by modification of the sampling procedure prior to use of the water injection test to determine void content.

2. To study the relationship of water content to standard test data reported as percent air and compressive strength.

3. To study the relationship between moisture contents of good service record Alden aggregate concrete and poor service record Otis aggregate concrete in order to detect changes in behavior that may be related to the service record.

4. To study how information pertaining to the moisture content of the highways may suggest changes in current testing procedures to improve criteria for evaluation of highway performance.

This program was undertaken as a cooperative effort with the Iowa State Highway Commission Testing Laboratory. The Laboratory provided the cores,

and determined percent air and compressive strength test results. The test results from the laboratory are presented as an Appendix to this report. The function of our group was to evaluate these data.

The sampling procedure called for three cores taken from each highway slab sampled. Two of the cores were handled according to standard procedure to serve as a control for special handling of the third core. The special core was kept wet until the percent air was determined. A two-hour soak preceded the percent air determination to fill the larger voids. This determination estimates the air filled fraction of air entrainment sized voids. After testing the core is dried and then soaked prior to testing for percent air. It is assumed that drying removes the water from air entrainment sized voids and that this second percent air determination estimates the total volume of air entrainment sized voids. Since the percent of air filled voids and the total percent of voids has been determined experimentally, the percent of water filled voids can be calculated as the difference in these values. These calculated quantities and others necessary for the evaluation of these data are shown in Table VII.

Highway Moisture Contents

The first part of the program was to determine whether water content of the highway could be measured by this method. Evidence supporting the proposition that it can be measured is as follows:

TABLE VII -- AIR, STRENGTH, AND WATER DATA

Core Identification	Special Test Method* A % of not dried	A % dried	ASTM Method** B % dried	C % dried	% Plastic Air	Compressive Strength B psi	C psi	Ave psi	% Water in H'way	% Saturation of H'way	Age at Test Time	Cement Source
CD-66-38-38	0.91	2.4	1.7	1.4		7820	7920	7870	1.5	62.1	28	Dewey
CD-66-41-1	0.30	1.8	1.7	____		9200	10,000	9600	1.5	83.3	25	Penn Dixie
CD-66-46-1	0.70	2.7	____	2.2		9745	8785	9265	2.0	74.1	20	Dewey
CD-66-48--	0.20	2.6	1.9	2.2		9520	10,105	9813	2.4	92.3	18	Dewey
CD-66-48-3	2.0	4.4	3.6	4.1		8045	8775	8410	2.4	54.6	18	Dewey
CD-66-48-84	1.7	2.6	2.0	2.2		6620	7120	6870	0.9	34.6	18	Dewey
CD-66-48-151	2.6	4.9	4.6	4.0	4.4	7720	8045	7883	2.3	46.9	18	Dewey
CD-66-50-151	0.6	3.8	3.2	3.2	4.4	8225	8775	8500	3.2	84.2	16	Dewey
CD-66-51-W	1.4	3.3	____	2.9		9030	7280	8155	1.9	57.6	15	Dewey
CD-66-52-1	31.	5.6	4.6	5.2	4.0	8590	9080	8835	2.5	44.6	14	Dewey
CD-66-56-218	2.0	5.2	4.0	4.2	4.9	8705	9665	9185	3.2	61.5	10	Dewey
CD-66-57-W	1.3	4.0	3.6	3.9	4.8	8595	8425	8510	2.7	67.5	9	Dewey
CD-66-58-150	1.0	3.7	2.1	2.2	4.0	7850	7915	7883	2.7	73.0	8	Penn Dixie
CD-66-61-150	1.6	5.3	4.4	4.4	6.2	7890	7730	7810	3.7	69.8	5	Dewey
A-66-29-01d 30	1.2	1.6	1.9	2.0		9539	9360	9448	0.4	25.0	37	Hawkeye
A-66-36-60	1.5	2.7	2.3	2.4		7405	7530	7468	1.2	44.4	30	Penn Dixie
A-66-41-14	1.5	2.3	2.4	1.6		8175	8170	8173	0.8	34.8	25	Penn Dixie
A-66-50-14	1.8	2.8	3.1	3.0		7150	7735	7443	1.0	35.7	16	Dewey
A-66-51-6	2.0	3.0	2.8	2.9		7175	8475	7825	1.0	33.3	15	Hawkeye
A-66-51-383	1.2	2.4	2.5	2.7		6550	6605	6578	1.2	50.0	15	Penn Dixie
A-66-65-65	1.6	6.9	7.5	7.6		6050	6205	6128	5.3	76.8	1	____

*Special test method of "A" designated cores required 2-hour soaking prior to air test.

**ASTM method of air test was run on "B" and "C" designated cores after compressive strength test.

1. Figure 7 shows the relationship between total void volume determined by the special and standard method for cores taken from the same slab. If perfect agreement existed all volumes would lie along the line. There appears to be a systematic difference which cuases the special core values to average perhaps 1/2 percent higher. These differences may be caused by one or more of the following reasons:

   a. Standard tests are made on short faced cores so that the materials are systematically different.

   b. Prior water injection may have opened the structure and permitted more thorough drying of the special cores.

   c. Fractures generated in evaluation of compressive strength may have intersected some trapped voids in the standard test and thus reduced void volume measured by allowing voids to be filled with water during soaking.

   In any event the total void volumes are sufficiently close to assume trends developed by the data are valid.

2. Figure 8 shows the trend of total void volume with time. Although there is some scatter the general tendency for the volume to decrease with time is evident. Since the younger concretes have been designed to have steadily increasing air contents, this result is not unexpected. It should be noted that non-air entrained cores follow the same trend.

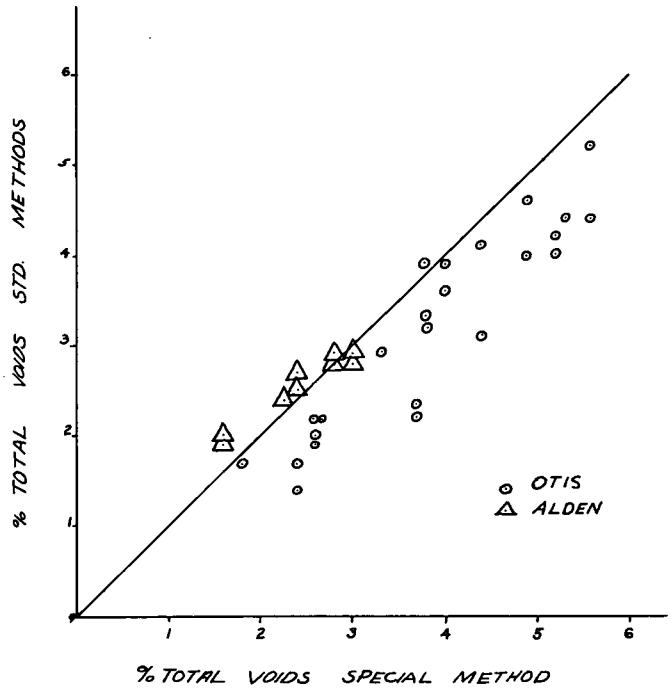


FIGURE 7. RELATIONSHIP OF TOTAL VOID VOLUME DETERMINED BY SPECIAL AND STANDARD ASTM METHODS.

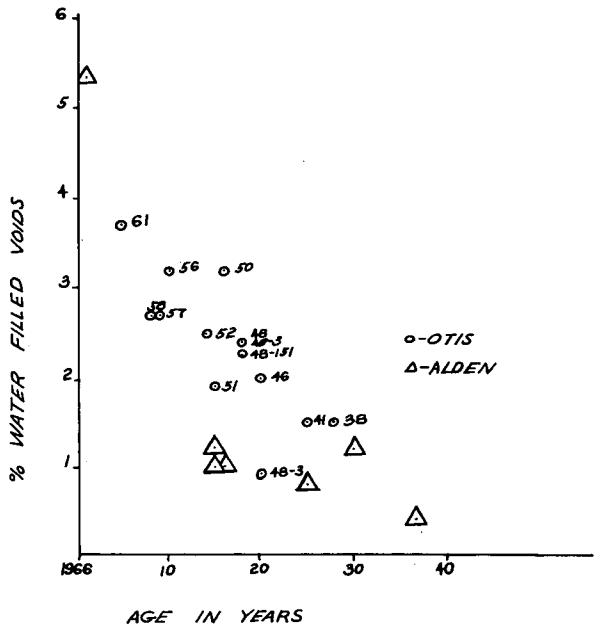


FIGURE 9. TREND OF PERCENT WATER FILLED VOIDS WITH TIME.

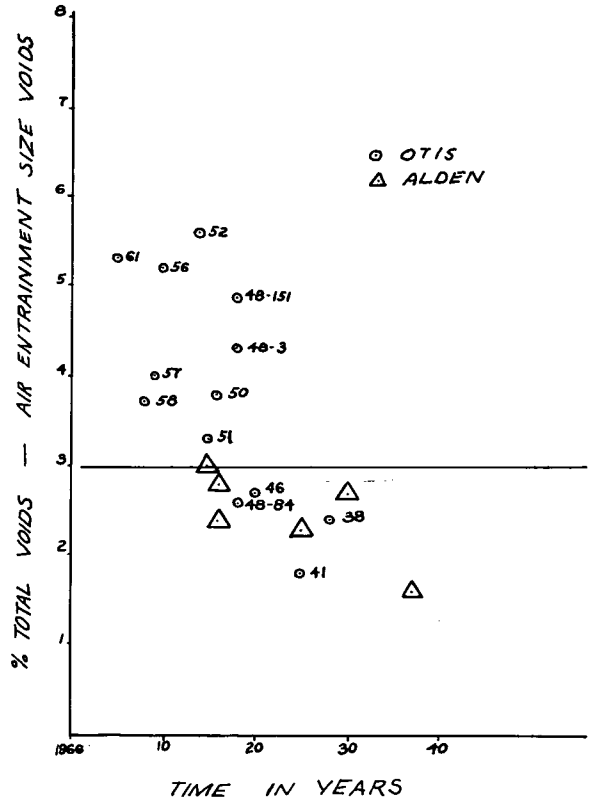


FIGURE 8. TREND OF TOTAL VOID VOLUME WITH TIME.

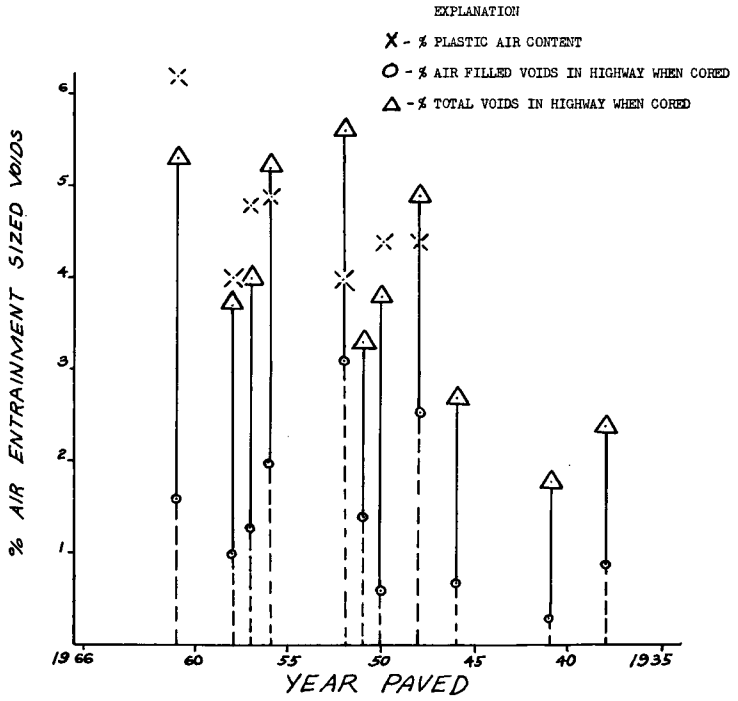


FIGURE 10. PARTITION OF AIR ENTRAINMENT SIZED VOIDS WITH TIME FOR ORIS AGGREGATE CONCRETE.

NOTE: 1. AIR SPECIFICATIONS 1960— 7%
1956— 6%
1952— 5%
2. WATER PRESENT IN VOIDS IN HIGHWAY WHEN CORED(% WATER FILLED) IS SHOWN AS LENGTH OF SOLID LINE ——.
3. AIR PRESENT IN HIGHWAY (% AIR FILLED) WHEN CORED IS SHOWN BY DOTTED LINE — — —.
4. SAMPLES 48, 48-84, 48-3 ARE NOT SHOWN.
5. TOTAL AIR IS VOID VOLUME DETERMINED BY WATER INJECTION.
6. PLASTIC AIR OBTAINED FROM CONCRETE PAVEMENT HISTORY CARDS.

3. Figure 9 shows the trend of percent water fraction with time. It makes the same general trend as total percent voids with time. Since this is not a random number and because it is reasonable for percent water to correlate well with percent voids, it is concluded that these values estimate the water present in the highway when the material was sampled.

Partition of Total Voids

Partition of the total void volume into the percent water filled and percent air filled fractions is shown in Figure 10. In addition, plastic air values are shown for the air entrained concrete cores. It should be noted that air entrainment appears to slightly increase the air content in cores but that the water filled fraction of the core increases with air entrainment. The immediate effect of air entrainment is to create a larger number of water-filled voids.

The Relationship of Air Content Specifications to Freeze and Thaw Behavior

The air filled fraction change with time is shown in Figure 11. This does not show any obvious trend with time. Most values are in a broad band 1 to 3 percent air. It should be noted that a group of Otis aggregate concrete samples have values of less than 1%. These will be discussed later.

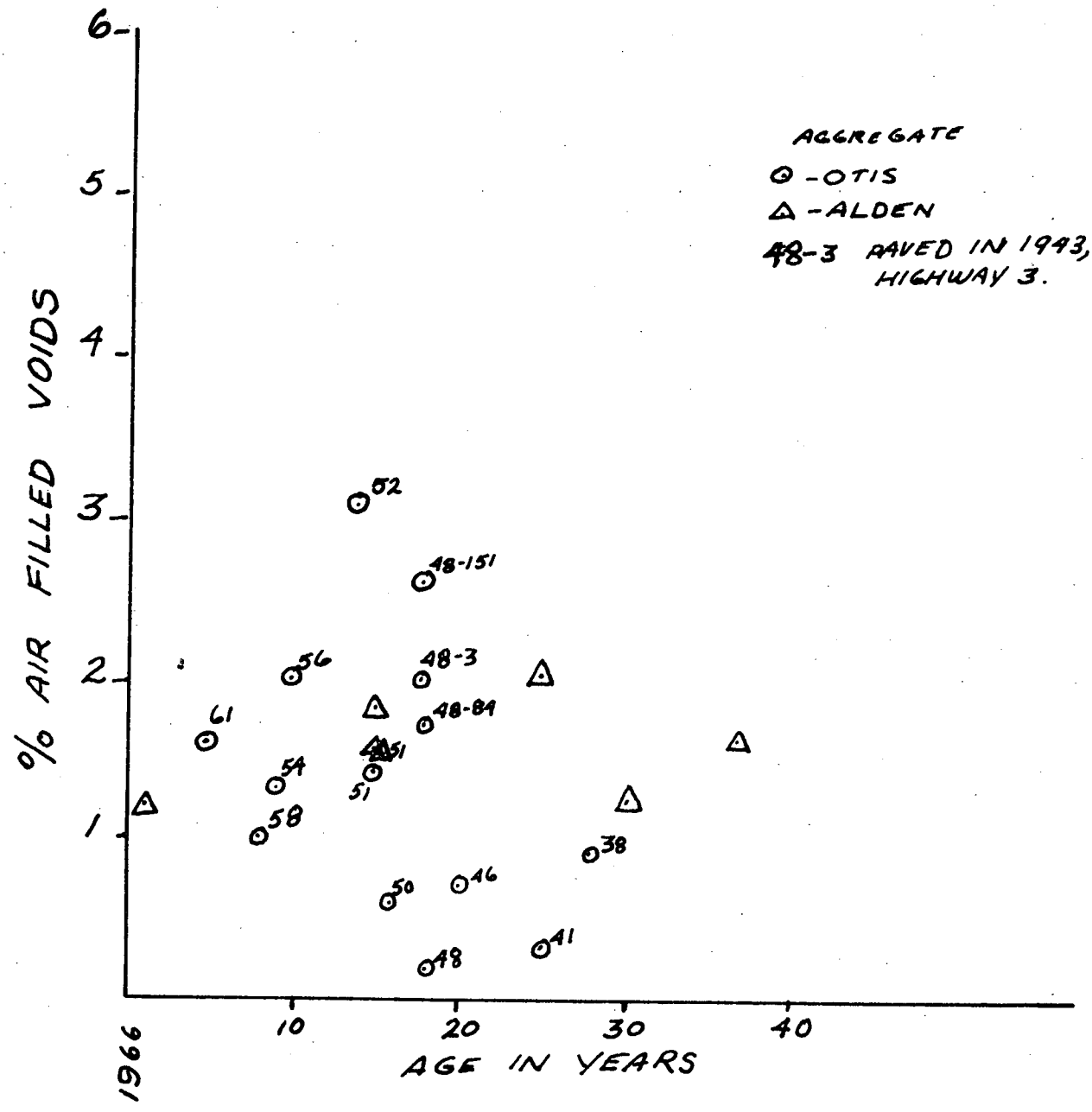


FIGURE 11. RELATIONSHIP OF AIR FILLED VOIDS WITH TIME.

As of this time of testing it is difficult to interpret these data in the light of the increase of the percent air specifications given as follows:

1960	7%
1956	6%
1952	5%

Initially it appears that the more air specified, the less air actually present in air entrained highway cores since these data show many of these voids are filled with water. This filling with water is reasonable in the light of theories of capillary attraction of very small voids and leaves little doubt that the water is present now at the time of testing. However, the trend developed with time shows that the percent water filled fraction decreases. When this water is replaced by air the actual air content becomes higher than would be expected for non-air entrained concrete. The other important trend is that the total void volume decreases with time in non-air entrained cores. Water expands about 9% therefore the total volume of air required (air filled fraction) would be in excess of the water filled fraction divided by 0.91 at all times. This excess would be available to contain water present in larger voids. The exact calculations are complicated by factors not covered in this study, namely the amount of water expected in large voids, distribution of water, diffusion rates of water and mean path of diffusion. However, one fact remains clear: if there is no excess, there is no freeze-thaw protection. This study only serves to point out two danger points during the life of the concrete. 1) If air specifications are too high, the high initial water fraction may promote freeze and thaw damage. 2) If the air specifica-

tions are too low, filling of voids more rapidly than water is removed may reduce the air fraction to a point where freeze and thaw damage may occur.

Although the method of determining the partition of the air filled and water filled fraction does not give information as to the excess air required, it does serve as a measure of the excess present at any time. It is recommended that adoption of the particular procedure for reactive air tests would provide information as to the relative freeze-thaw resistance of the highway matrix by serving as an index to excess air present. Correlation of these excess air values with freeze and thaw performance of highways sampled should provide some empirical measure of the amount of excess air required by Iowa highways to impart freeze and thaw resistance. Once the requirement for excess air is established this number could serve as one criteria for establishment of meaningful specification on initial air content.

Table VIII serves as an illustration of the change in excess air content for Otis aggregate concrete. It should be noted that one sample is particularly vulnerable to freeze and thaw damage since it does not have room for the water normally contained in air entrainment sized voids. Some others have so little excess air as to be of doubtful value in prevention of freeze and thaw damage in larger voids.

TABLE VIII . Partition of void volume in Otis aggregate concrete

YEAR PAVED	% TOTAL VOIDS	% AIR FILLED VOIDS	% WATER FILLED VOIDS	% ICE FILLED VOIDS*	% EXCESS AIR**
38	2.4	0.9	1.5	1.65	0.7
41	1.8	0.3	1.5	1.65	0.1
46	2.7	0.7	2.0	2.2	0.5
48	2.6	0.2	2.4	2.64	0
483	4.4	2.0	2.4	2.64	1.8
48-84	2.6	1.7	0.9	0.99	1.6
48-151	4.9	2.6	2.3	2.53	2.4
50-151	3.8	0.6	3.2	3.52	0.3
51	3.3	1.4	1.9	2.09	1.2
52	5.6	3.1	2.5	2.75	2.8
56	5.2	1.3	3.9	4.3	0.9
57	4.0	1.4	2.6	2.86	1.1
58	3.7	1.0	2.7	2.97	0.7
61	5.3	1.6	3.7	4.07	1.2

* The volume which will be formed from the water present in voids obtained dividing percent water filled voids by .91.

** Percent excess air is the air present in excess of that required for the volume of ice formed from the water normally present in air entrainment sized voids. This excess is the maximum space available to sustain the increase in volume due to freezing of water in larger voids. Percent excess voids will always be less than percent air filled voids and is obtained by subtracting percent ice filled voids from percent total voids.

Relationship of the Void Volume, Air Content and Water Content to the Compressive Strength of Alden Aggregate Concrete

Alden material has a good service record and thus serves as a control for evaluation of changes in poor service record Otis material. Figure 12 shows the relationship between the individual compressive strength and total percent voids for Alden material. The higher strengths are associated with lower void contents but the change is too erratic over the small range in values to provide a functional relationship.

Figure 13 shows the relationship between average strength and the percent air filled fraction of air entrainment sized voids. Again the erratic vertical range of these data denises a functional relationship.

Figure 14 shows the relationship between average strength and percent water filled fraction of voids. Unlike other plots a decrease in water content appears to be associated with an increase in compressive strength in a consistent manner. Unfortunately the useful range of interest is only 0.8%. Since slight differences in water content mean large changes in strength, the relationship is too sensitive to experimental error to be useful as a quality control chart of the aging of this highway material. A more useful relationship is shown in Figure 15 which relates percent saturation of Alden material to average compressive strength. For these purposes the percent saturation is defined as the percent water filled fraction divided by percent total voids multiplied by 100. This relationship has sufficient consistency over a range of 55% to serve as a useful quality control function. For Alden material it associates a decrease in percent saturation with an increase in average compressive strength.

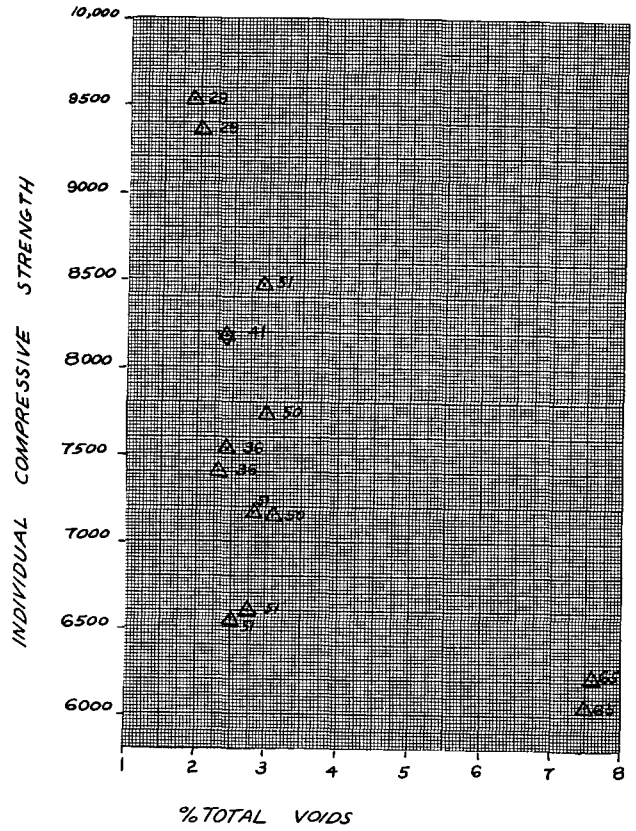


FIGURE 12. RELATIONSHIP OF COMPRESSIVE STRENGTH AND TOTAL VOIDS FOR ALDEN AGGREGATE CONCRETE.

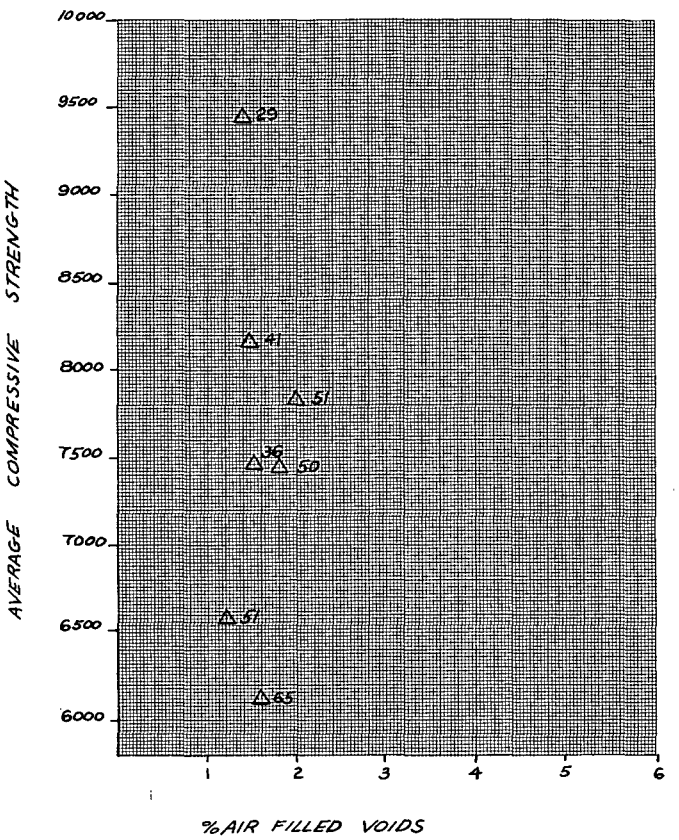


FIGURE 13. RELATIONSHIP OF AVERAGE COMPRESSIVE STRENGTH AND PERCENT AIRFILLED VOIDS IN ALDEN AGGREGATE CONCRETE.

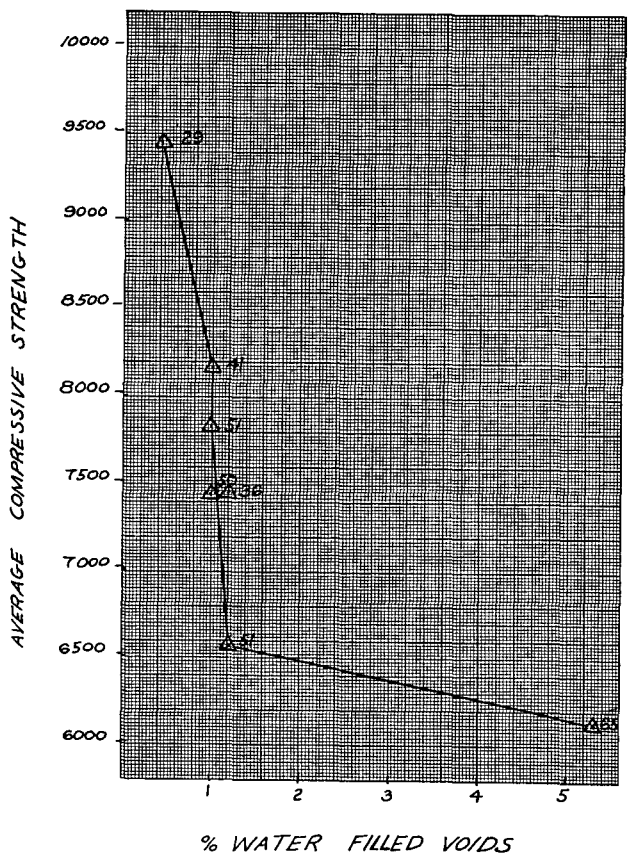


FIGURE 14. RELATIONSHIP OF AVERAGE COMPRESSIVE STRENGTH AND PERCENT WATER FILLED VOIDS IN ALDEN AGGREGATE CONCRETE.

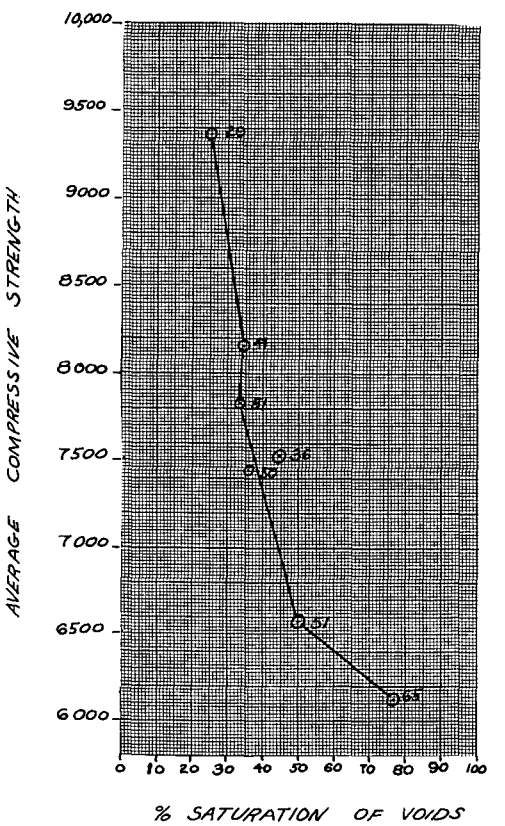


FIGURE 15. RELATIONSHIP OF AVERAGE COMPRESSIVE STRENGTH TO PERCENT SATURATION IN ALDEN AGGREGATE CONCRETE.

Relationship of the Void Volume, Air Content and Water Content to the Compressive Strength of Otis Aggregate Concrete

Figure 16 shows the relationship of individual compressive strength to total void volume for the poor service record Otis aggregate concrete material. Like Alden material it shows no definite trend for this plot.

Figure 17 shows the relationship of average compressive strengths to percent air filled voids. Like the Alden material it presents no useable trend. Unlike the Alden in which the percent air appears to approach a constant value, the Otis material displays a general trend of higher strengths at lower percent air values.

Figure 18 shows the relationship of average compressive strength to percent water filled voids. Unlike Alden material, which shows an increase in strength associated with a decrease in water content over a limited range, the Otis material shows a scatter of the data.

Figure 19 shows the relationship of average compressive strength to the percent saturation for Otis material. The air entrained material still shows considerable scatter, however the non-air entrained material displays a definite trend with percent saturation. This trend seems to be followed by the air entrained material also; however, the air entrained data are more erratic. It should be noted that although percent saturation -vs- strength curves seem to describe a consistent behavior within one aggregate concrete system, the behavior of the two systems are different. The differences will be discussed later. At this point only the differences will be summarized.

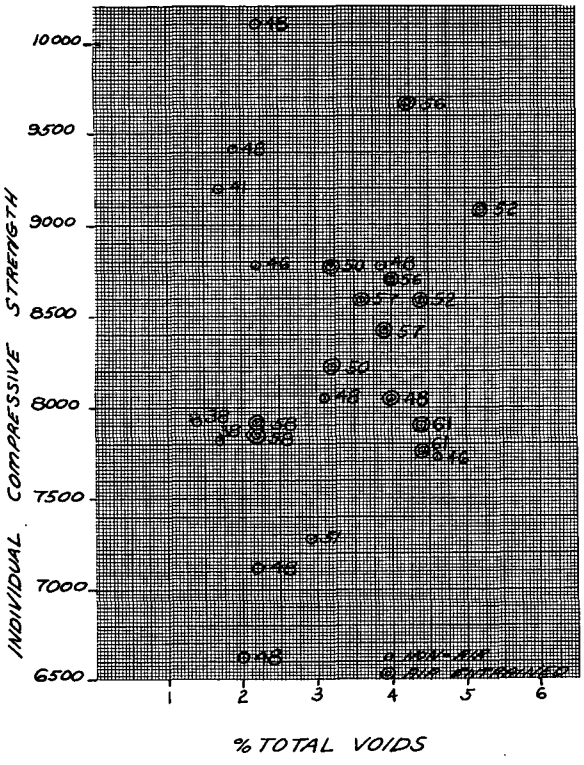


FIGURE 16. RELATIONSHIP OF COMPRESSIVE STRENGTH TO TOTAL VOID VOLUME IN OTIS AGGREGATE CONCRETE.

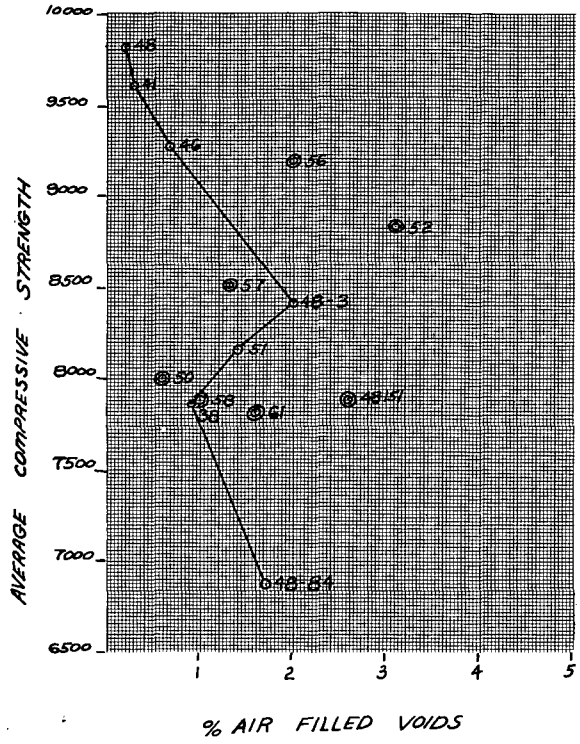


FIGURE 17. RELATIONSHIP OF AVERAGE COMPRESSIVE STRENGTH TO PERCENT AIR FILLED VOIDS IN OTIS AGGREGATE CONCRETE.

⊙ NON-AIR ENTRAINED
◎ AIR ENTRAINED

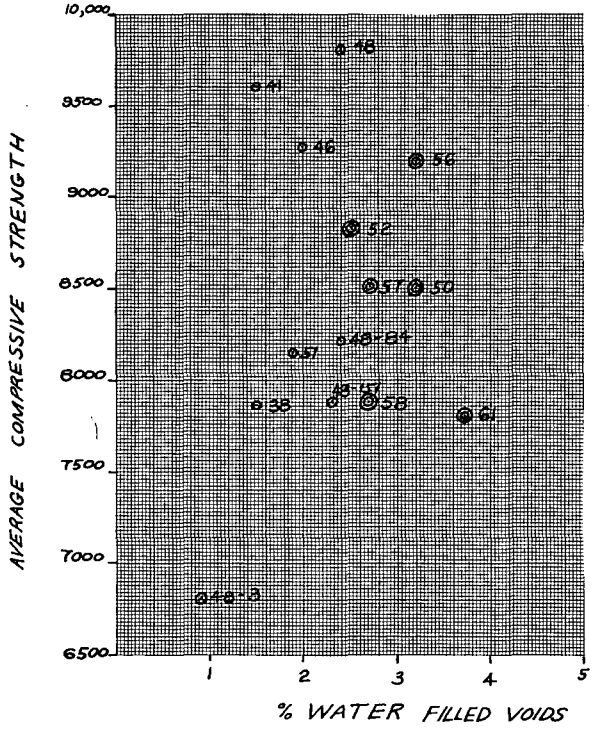


FIGURE 18. RELATIONSHIP OF AVERAGE COMPRESSIVE STRENGTH TO PERCENT WATER FILLED VOIDS IN OTIS AGGREGATE CONCRETE.

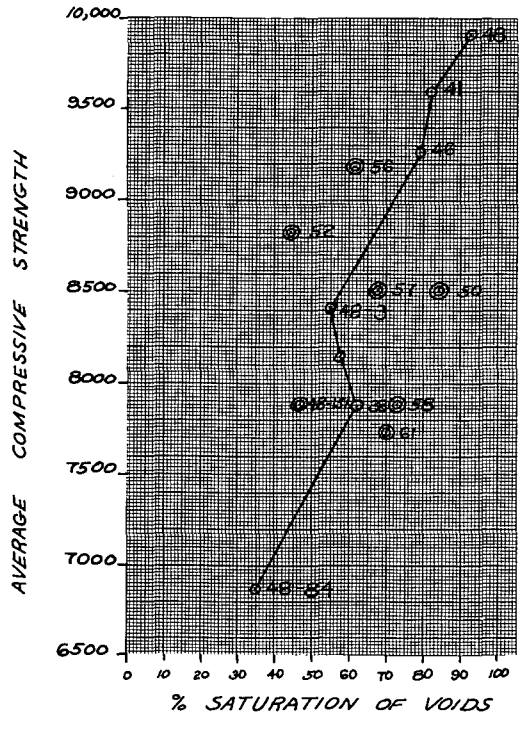


FIGURE 19. RELATIONSHIP OF AVERAGE COMPRESSIVE STRENGTH TO PERCENT SATURATION OF OTIS AGGREGATE CONCRETE.

Summary of Differences in Alden and Otis Material Behavior

1. Alden Material (good service record)
   a. Percent saturation -vs- strength curve associates high compressive strengths with low percent saturation.
   b. The percent saturation -vs- strength curve reflects the trend in the water filled fraction -vs- strength data.

2. Otis Material (poor service record)
   a. Percent saturation -vs- strength curve associates high compressive strength with high percent saturation.
   b. The percent saturation -vs- strength curve reflects the trend in the percent air filled fraction -vs- strength data.

Review of HR-86 Strength Versus Time Data and Additional Justification of HR-86 Assumptions

In HR-86 compressive strength data was interpreted in the light of the aggregate-matrix breaking study. Conclusions were drawn that the data from 1963 cores showed a strength dependence which correlated with age, source of cement and source of coarse aggregate. The strength of highways older than 5 years correlated best with aggregate. Although this conclusion fits the data, it was based on the assumption that concrete made from the same source material at different times would have an average characteristic strength

at a certain age. It was reasoned that if differences in compressive strength formed by repeated sampling of the same slab followed the trends established by cores of different highways sampled in 1963 then the assumption holds for 1963 data trends. Additional points needed to define the trend for the Otis material were sampled in 1966 under HR-116.

Figure 20 strength -vs- time is shown for Alden aggregate concrete material. Both the 1963 and 1966 data display a general increase in strength with time for Alden material. The maximum strength developed in 37-year-old samples only averages 9500 psia. It should be noted that dashed lines connecting the data points representing the 1963 and 1966 data connect samples from the same highway slab. The results of compressive strength tests for Otis aggregate concrete cores are shown in Figure 21. It should be noted that dashed lines connecting data points representing 1963 and 1966 data on the same slab follow the inverted U shape established by data points from different highways. The shape of the curve will be discussed in a following section. At this point it is only necessary to note that the assumption that behavior of strength -vs- time in one highway could be approximated by behavior of strength -vs- time in different highways is valid.

Strength Versus Time Relationship for Otis Aggregate Concrete

Figure 21 shows the expected strength -vs- time relationship as a large inverted U shape. Several cores appear not to follow the general trend. The

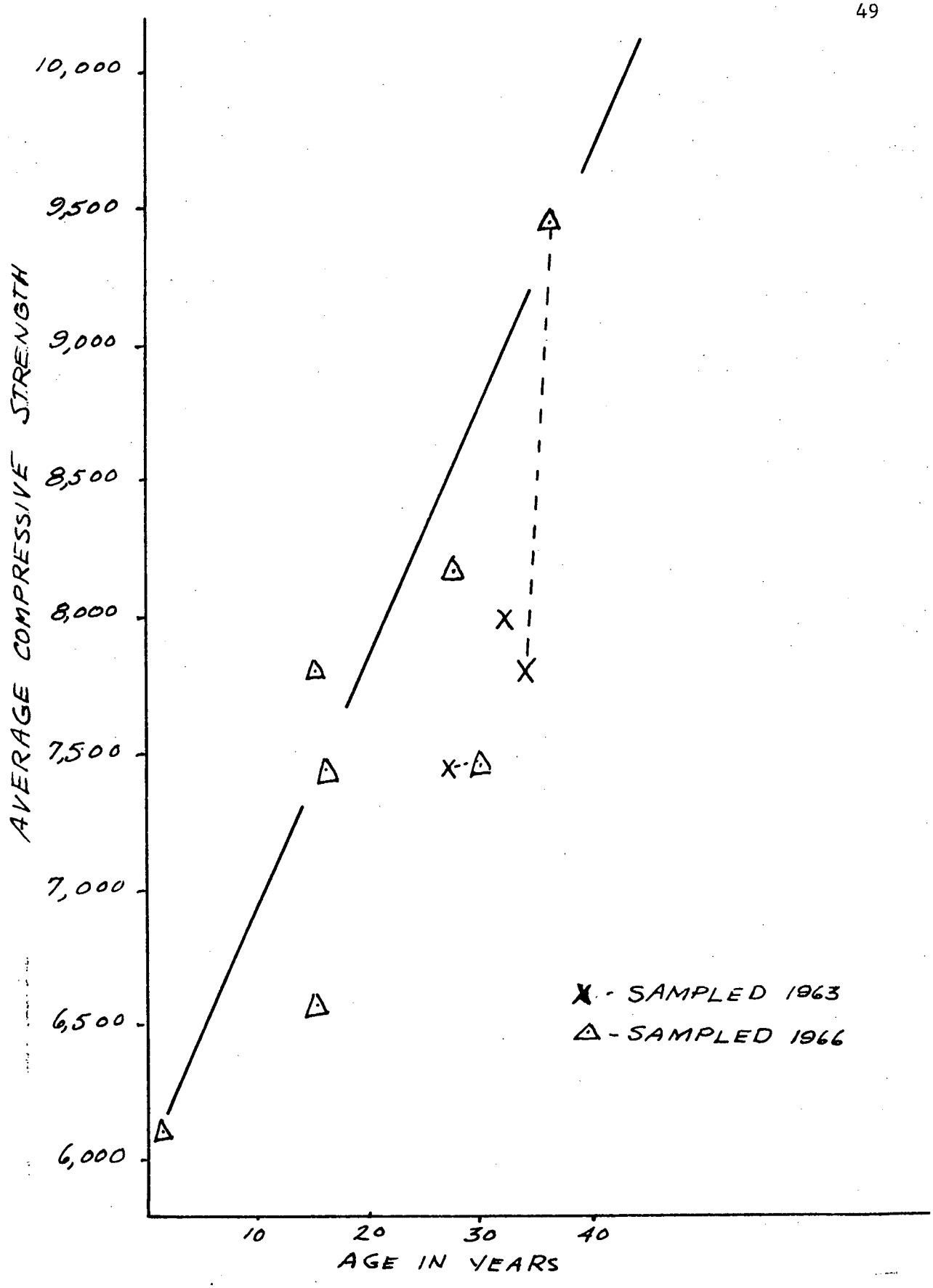


FIGURE 20. RELATIONSHIP OF COMPRESSIVE STRENGTH AND TIME FOR ALDEN AGGREGATE CONCRETE

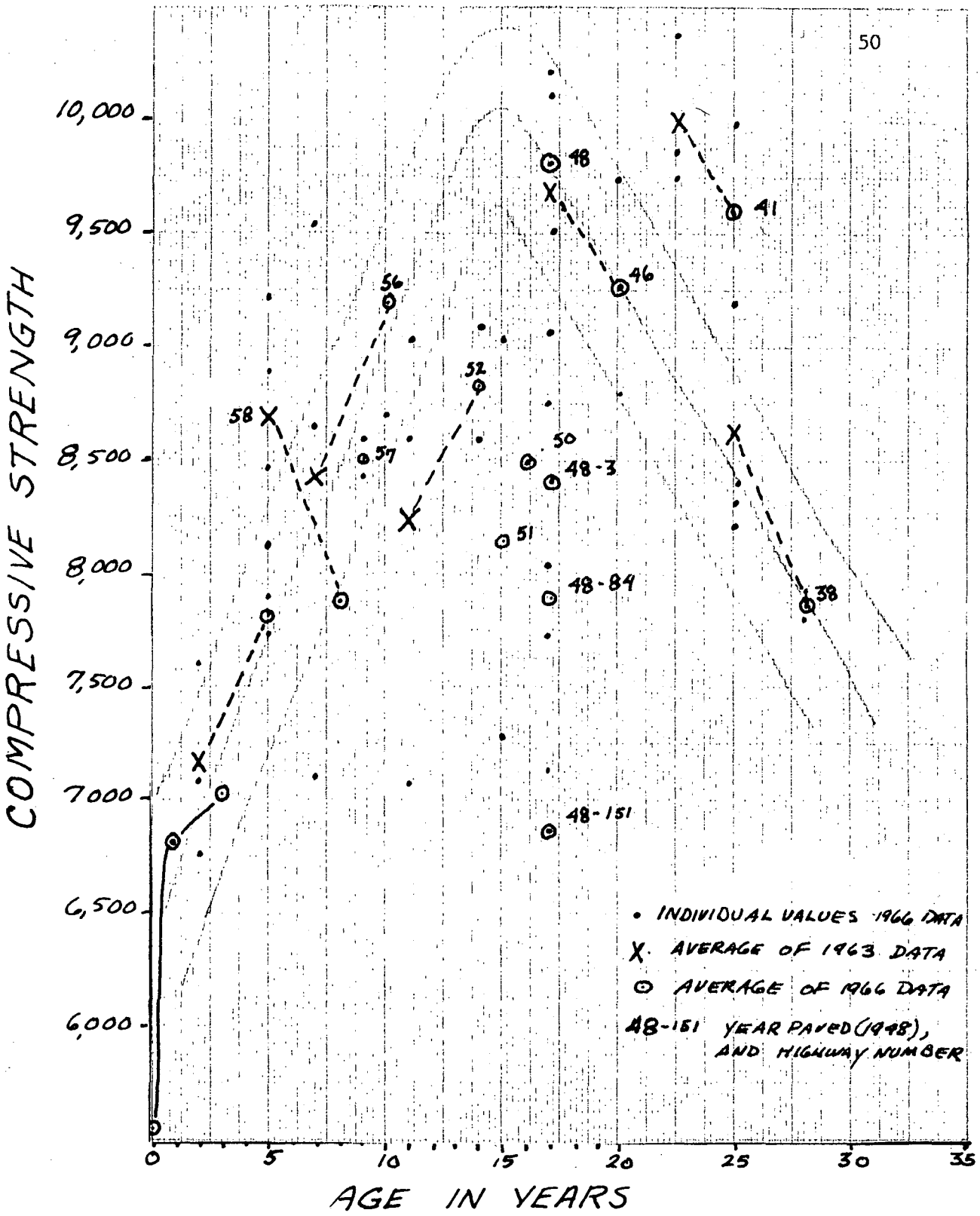


FIGURE 21. RELATIONSHIP OF COMPRESSIVE STRENGTH AND TIME FOR OTIS AGGREGATE CONCRETE SAMPLED IN 1963 AND 1966.

band shown is presented with little experimental justification. Values accepted for the strength often differ by as much as 1000 psia for cores sampled from the same slab. It was reasoned that averages of two tests should be within $\pm$ 500 psia from any expected value for the slab. The band was established on this basis. Individual points as well as averages are shown. Note that the solid line connects averages for 28 days, 1 year and 3 years compressive strengths furnished by ISHC Testing Laboratory. This is in general agreement with the projected average of the U-shaped curve. The following exceptions to the curve are noted.

1. Point 58

   Although the average of the 1963 and 1966 points fall on the expected value, the direction of change between 1963 and 1966 is not that expected from the curve.

2. Point 52

   Although the direction and magnitude of the change in the 1963 to 1966 data are about as expected these points are offset from the expected curve. (Point 52 represents a highway which is failing more rapidly than expected from the service records of Otis material.)

3. Point 41

   Although the direction and magnitude of the change in the 1963 to 1966 data are about as expected these points are also offset from the curve. (Point 41 represents a highway constructed with Penn-Dixie cement that appears to be more durable than expected from the service records of Otis material.)

4. Points 50 and 48-151

   Are sampled from city slabs, with a deferred durability record.

5. Points 51, 48-84 and 48-3

   From an anomalous group.

Although only one band is shown it is expected that each group would follow a similar curve in which the U shape is displaced in time depending on the merits of the material. Periodic compressive testing of certain highways would establish the band behavior for a particular material. Since the maximum point on the curve is associated in time with the life expectancy of Otis highways obtained from service records, establishment of the band behavior through compressive testing would enable the highway engineer to predict the remaining life expected in the highway. Perhaps forecasts of this kind could be used to schedule covering of highways before major deterioration occurs. In any event if this band behavior, which is known for the Otis material, is common to other aggregate concrete systems, periodic testing should give sufficient warning that general maintainance could be scheduled.

In contemplating the design of a new highway it should be noted that compressive strength values test primarily breaking behavior of the aggregate-matrix bond for about the first five years. It is only after this time that the aggregate sensitive behavior becomes dominant. Thus it is expected that the aggregate controlled bond behavior would be evident only after the five year period. Early compressive tests (28 day, 1 year and 3 year tests) would not be expected to verify the design. Establishment of bands for older concrete systems and particularly the differences in bond behavior should

provide a basis for deciding how similar a proposed material is to one of known service record.

It cannot be too strongly emphasized that band behavior or maximum strength behavior has only been shown for the Otis aggregate concrete. Comparison with the Alden data show that the Alden material has not yet reached a maximum, if indeed a maximum exists in the Alden system.

Although we would like to recommend a comprehensive compressive test program which would provide the current status of the highway relative to its life expectancy in terms of its maximum compressive strength it is not yet feasible. We do recommend that some of the older highways sampled for HR-86 such as the Dubuque aggregate concretes for which compressive test values are known for a particular slab in 1963 be re-tested. Decreasing compressive strengths with time in these curves would be evidence supporting extension of maximum strength behavior to systems other than the Otis aggregate concrete system.

Possible Mechanism of Otis Concrete Compressive Strength Band Behavior

The following points have been reviewed in other sections of the report and serve as a basis for evaluation of Otis behavior.

1. Average compressive strength of both Alden and Otis materials have a linear dependence on percent saturation. As percent saturation increases the strength of Alden material decreases and the strength of Otis material increases.

2. In Alden material the percent saturation follows the trend of the water filled fraction.

3. In Otis material the percent saturation follows the trend of the air filled fraction.

4. Several Otis samples have very low excess air contents.

5. The average compressive strength of concrete initially depends on the source of cement for as long as 5 years.

6. Strength -vs- time dependence for Alden material indicates the material slowly grows stronger with time.

7. Strength -vs- time dependence for Otis material indicates the material rapidly grows stronger with time until a maximum is reached and then decreases in strength with time.

8. The Otis band behavior had several exceptions which were either displaced or did not fit the overall pattern.

This information will be brought to bear on the problem with the assistance of Figure 22 concerning percent saturation -vs- time which relates behavior to source of cement. Three sources of cement and both sources of coarse aggregate material are identified on this graph, the data for Dewey cement is broken into parts I, II, and III. All the Penn-Dixie material is shown as one curve with the exception of Otis point 41 which stands alone. The two Hawkeye points are connected. These points will be discussed separately.

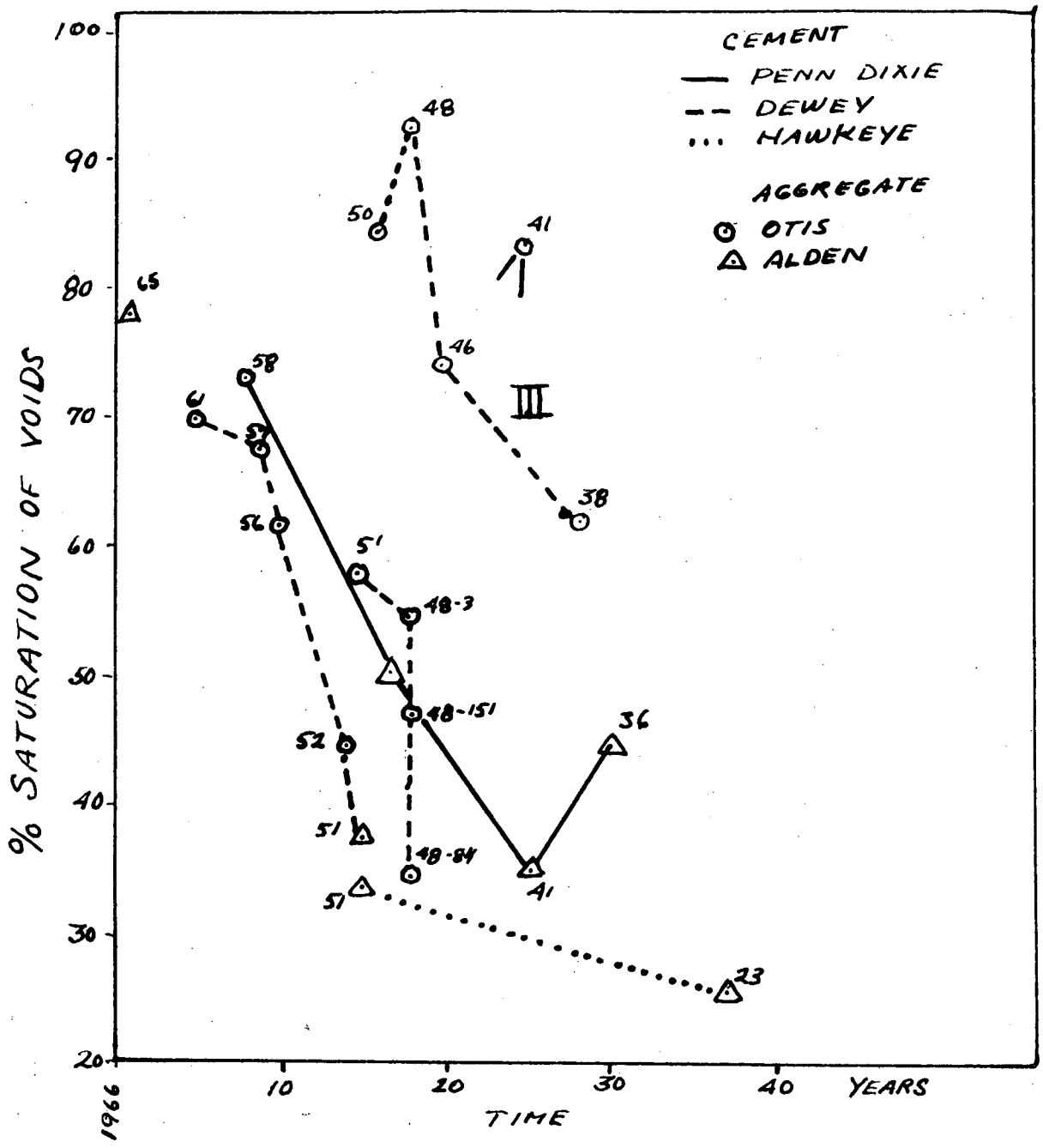


FIGURE 22. RELATIONSHIP OF PERCENT SATURATION WITH TIME ACCORDING TO CEMENT SOURCE.

Hawkeye Cement

Both points display the behavior of Alden material. These points show a decrease in percent saturation and an increase in strength with time which is characteristic of Alden aggregate concrete.

Penn-Dixie Cement

With the exception of point 36 the curve continues but Alden and Otis material shows a decrease in percent saturation with time. This correlates with an increase in strength displayed by the materials. Point 36 which is an anomalous high the percent saturation -vs- time curve is also an anomalous low on the strength -vs- time curve.

Dewey Point II

The points on this curve are a departure from the expected values. They act as if they were displaced from Part I curve. With the exception of the interchange of points 51 and 48-3 they show a reversed dependence of strength, namely as the percent saturation increases the strength increases. It contains only Otis samples.

Dewey Point III

Point three represents a radical departure from the expected value of Point I. It contains those Otis cores which show a decrease in strength and percent saturation with time.

Dewey Part I

The saturation -vs- time curve decreases with time strength values for this Otis material increase with time just as the Alden materials. All the data up to this point are consistent with a general decrease in percent saturation with time, a corresponding increase in strength with time proportional to the percent saturation and the differences in percent saturation at any one time being largely explained on the basis of initial cement.

This area of the figure also contains Point 41 (Penn-Dixie) cement that was shown to have decreasing strength with time behavior offset but similar to Dewey Part III behavior. It would seem from this point to point correlation the change in the strength -vs- time behavior of the Otis is related to the drastic increase in percent saturation of Dewey Part III materials. This indicates that mechanism by which the strength -vs- time dependence of Otis aggregate concrete is changed, must also change the percent saturation.

Saturation is calculated in this report is a ratio of the water filled fraction to the total voids. Changes in the saturation value reflect changes in one or both of the quantities. Figure 23 shows the pattern of changes in the Dewey Part III samples for compressive strength, percent saturation, water fraction and total voids. By matching patterns it is obvious that changes in total void volume control the percent saturation and strength behavior of these Otis materials. Low total void volumes are associated with high strength for these materials. Since the water fraction appears to be a decreasing value with time, the void volume must decrease at a faster rate than the water fraction to get the increase in percent saturation associated with

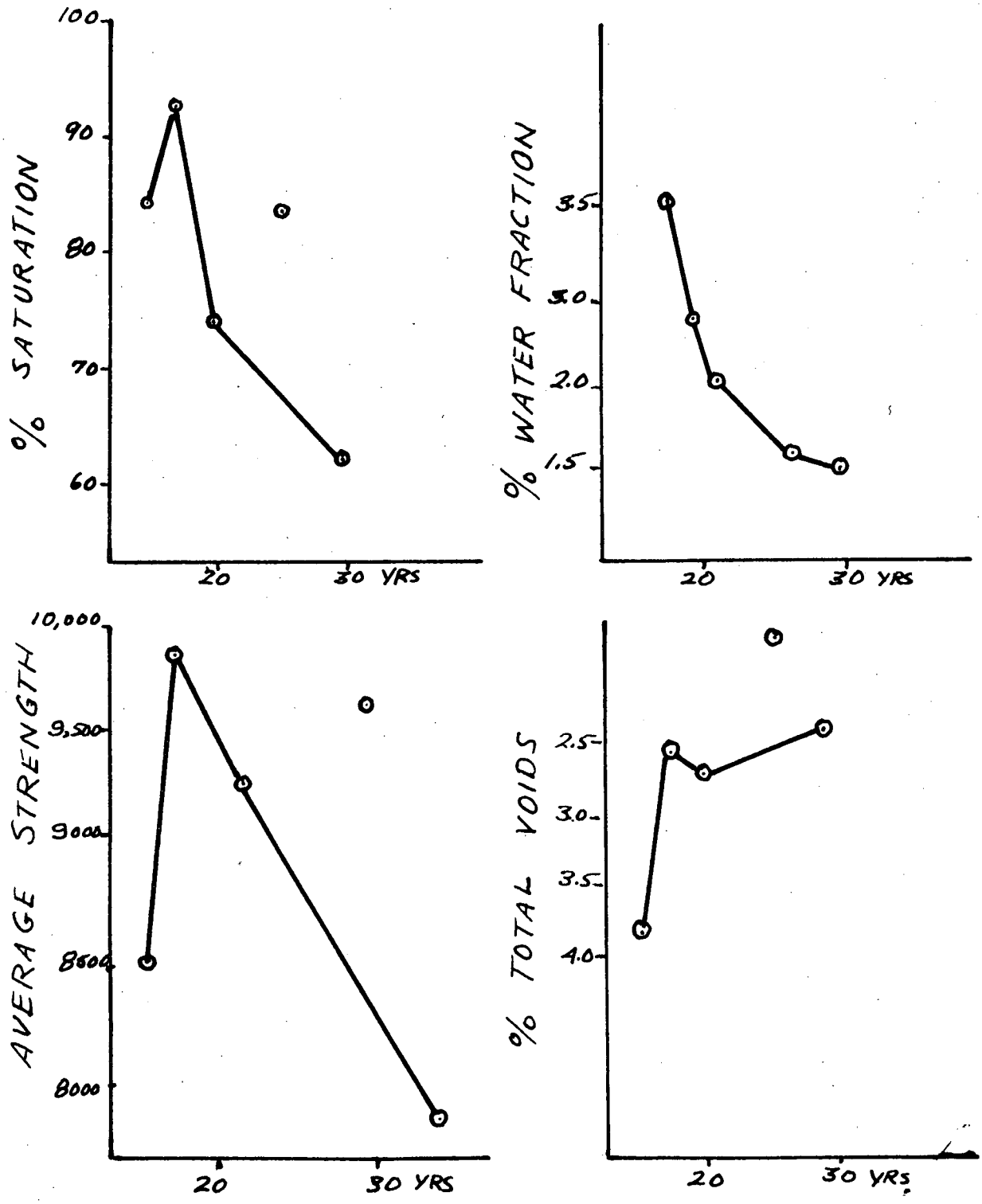


FIGURE 23. THE PATTERN OF CHANGES FOR DEWEY PART III SAMPLES SHOWN IN FIG. 22 WITH REGARD TO PERCENT SATURATION, WATER FILLED VOIDS, AVERAGE COMPRESSIVE STRENGTH AND PERCENT TOTAL VOIDS FOR OTIS AGGREGATE CONCRETE.

Dewey Part III samples. The mechanism which is consistent with this description of the observed behavior is a filling of the air entrained sized voids with a solid material. Since the behavior is associated with concretes constructed with Otis aggregate and not with those constructed with Alden aggregate it is reasonable to assume the source of the solid material is the Otis aggregate. The rate of leaching of the material may control the rate at which the voids are filled.

The onset of deterioration of the highway is also associated in time with the maximum strength developed in this sample. It should be remembered at this time that the excess air study showed that these particular samples afforded little protection against freeze and thaw damage. The explanation of the path of failure of Otis aggregate concrete which is consistent with all the observed data is as follows:

1. A gradual loss of water with time.
2. A gain in solids leached from the coarse aggregate.
3. Reaching a critical percent saturation.
4. Failure by freeze and thaw action.
5. A decrease in percent saturation due to isolated microfractures generated by freezing and thawing action.

The expected life of the highway depends on when the critical saturation is reached. This in turn depends on the initial void present, the rate at which water is lost and the rate at which leaching of the coarse aggregate fills the voids and the presence of leachable material. Design on the basis

of this information is difficult since the factors are interrelated. For example, increases in the total void content by addition of air also increases the leaching rate. Since these factors oppose each other it is difficult to say how much or if the life expectancy has been improved without testing.

The next step in solving the Otis problem and in generalizing the problem to cover other poor aggregate sources of this type appears to be the detection of the kind of material which is filling the voids and subsequent reduction of such material at the time of paving. Until this can be accomplished percent saturation and particularly the dependence of strength on percent saturation appear to be related to the useful life of the highway. Ninety percent saturation appears to be a critical number associated with freeze and thaw damage. The strength dependence of percent saturation give information as to whether the damage has already occurred. Increasing strength with increasing percent saturation may be considered a symptom of a concrete's susceptibility to deterioration.

Freeze and thaw testing is usually associated with behavior of the coarse aggregate. In this study it was evident that the matrix may also be susceptible to freeze and thaw action. The percent saturation of this study applies only to the problem of the matrix.

PRELIMINARY INVESTIGATIONS FOR HR-116

Introduction

One of the areas of research was to contrast the behavior of Otis aggregate concrete from the center of the slab and from locations near the highway joints. This information was to be compared with expected behavior forecast by HR-86 studies and changes evaluated in the light of similar information obtained from a good service record highway system containing Alden aggregate concrete. A historical approach is presented in this section to show how and why we became interested in the kinds of information which describe the concrete behavior. The subjects covered in this section include the following:

1. Survey of highway records and sampling.
2. Evaluation of studies on individual pieces of deterioration zone concrete.
3. Program developed from study of individual pieces of deterioration zone concrete.
    a. Evaluation of near surface changes leading to acetate peel techniques.
    b. Evaluation of brown filings leading to rim studies.
    c. Evaluation of near surface changes leading to additional chemical studies.

Survey of Highway Records to Locate HR-116 Core Samples

Twenty-five highway sites were selected from initial construction records as possible sources of Otis highway material. Field check of highways

under consideration narrowed choices to the fifteen sites cored. Loose material in the form of individual pieces of concrete collected from the selected highways during the field trip served as preliminary samples to develop methods of investigation suitable for the petrographic fence study. Study of the Alden records resulted in a similar field trip and selection of eight highway sites to act as a control for the Otis study. Despite this selection process the number of Otis locations sampled was reduced to fourteen because one set of cores was later found to be River Products material and the number of Alden locations sampled was reduced to seven since one core set was found to consist of gravel coarse aggregate.

Evaluation of Individual Pieces of Deterioration Zone Concrete

The concrete fragments obtained during the survey of the highways prior to the coring of the highways were studied petrographically. Samples were sawed perpendicular to the highway surface so the contrast in surface and bulk properties of the materials could be compared. Gross examination of the pieces and slices showed consistency in the following observations.

1. The matrix which composed the top ½-inch of the sample appeared lighter in color than the bulk matrix material. This zone containing the change was commonly separated from the lower bulk matrix material by minor fractures. The fractures can be also considered to form the undulating irregular upper surface or limit of coarse aggregate material. The lighter colored matrix material was also studied under transmitted light and found

to be more birefringent under crossed nicols than the bulk matrix material.

2. A brown surface film was associated with both matrix and aggregate fracture surfaces.

3. Inner rims of certain coarse aggregates were marked with fracture patterns which connected to the major fracture patterns of the sample.

4. Fibers with a spiral morphology similar to that described in the literature for toberomorite and brucite have diameters similar to the minor fracture zones and these fibers or fiber bundles have lengths up to a few millimeters. The diameter of the bundles are in the order of 10 microns. It is suspected that these fibers are not brucite since they appear insoluble in N_3HCl solution.

Study of near surface matrix changes

Evaluation of near surface changes in the loose samples pointed out the need for a means of study of large areas of concrete under transmitted light to follow the nature of the boundaries within the surface zone. To meet this need a technique using acetate peels originally developed for use in petrographic examination of carbonate rock was adapted to the highway concrete system. Smooth surface slices of concrete are replicated in acetate to show the surface morphology and the acetate mounted in 3 ¼ x 4 ¼ polaroid slide mounts (#633) which are suitable for projection as lantern slides or direct observation under the petrographic microscope. This mount gives a viewing area of 2 ½ x 3 ¼ inches which is six times the area of the studied 1 x 1 ½ thin sections. Since the replica does not contain the concrete material it cannot be used for crossed nicol studies. However, if the surface is treated with hydrochloric acid prior to peeling the acid soluble materials

are removed on the peel surface. Such peels show a high birefringence of the matrix material in the surface zone of concrete as contrasted with the matrix of the lower bulk material. Starting with a sawed surface peels can be produced at a rate of about 5 per hour at a fraction of the cost of thin sections. Because of the low cost, large area sampled, and rapid rate of production acetate peels have replaced the need of thin sections for most of the observations in the general petrographic transmitted light observations of HR-116. In other more mineralogically oriented studies of concrete, acetate peels may be used to locate the sensitive zones requiring thin section study since the thin film removed on the peel does not destroy the feature sampled but serves as a map of its location on the sawed surface.

Brown surface stain study

Evaluation of brown iron films on fracture surfaces of all particles and prior rim studies resulted in the investigation of the mobility of iron in the natural highway concrete system. A technique using potassium ferricyanide developed to detect ferrous iron in dolomites was adopted to highway concretes. This stain detects ferrous (Fe^{++}) iron as a blue zone in slightly acid soluble material. A different stain potassium ferrocyanide will detect both ferrous (Fe^{++}) and ferric (Fe^{+++}) iron as a similar blue zone. Acetate peels of the stained surface serve as a map of the iron rich zones of the concrete slice. In this procedure a surface is stained for ferrous iron, peeled, the stain removed by mechanical polishing, and then stained for total iron and peeled. Comparison of iron distributions on the two acetate peels determines preferential zonation of the Fe^{++} or Fe^{+++} forms.

Petrographic study of Otis rimmed aggregate had previously shown that iron was depleted in the rim zone. Application of the repeated staining acetate peel technique to these samples demonstrated that the Fe^{++} present throughout the rock was converted to Fe^{+++} in the reaction rim. This observation implies that an oxidation-reduction reaction is part of the rim forming process. Further observation of rimmed Otis aggregate in the deteriorated core sample of CD-48 using the repeated staining acetate peel technique established a relationship between location of fractures and rim zones. Fractures occur subparallel to the boundary of $Fe^{+++}$and Fe^{++} zones usually within the Fe^{+++} zone. Such a fracture pattern creates a picture frame failure zone. This pattern is similar to that shown by G. M. Idorn of Denmark as characteristic of drying shrinkage failure.

These observations are interpreted as establishing a positive correlation between the particles which form rims and the path of fractures if the rimmed aggregate zone of the particle is weaker than the matrix. The presence of such aggregate types in the Otis material was shown in the breaking study of HR-86.

Although rims have been studied as special features of concrete, this is the first direct evidence that rim material represents the onion skins* found in deteriorated fracture zones. Such rim forming aggregate should be suspect as highway aggregate pending investigation of the strength of the rim zone.

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* term first used by Mr. Theodore Welp when he first called attention to this phenomena.

Evaluation of chemical data

Evaluation of the differences in the top matrix surface led to chemical tests of the matrix fraction of concrete slices containing the surface, ¼ inch depth and one inch depth of a CD-52 core sampled under HR-86. Since under HR-86 the CD-52 material was sampled only at the one inch, three inch and five inch depths the additional samples represent additional data points to detect possible near surface depth changes. Data points of the CD-52 preliminary run are shown for fine insoluble, soluble silica, CaO, MgO, Fe_2O_3, Na_2O, K_2O, fixed water, and CO_2 in figure 24. These points confirm the suspected near surface concentration differences. Because of these results, systematic chemical analyses of the matrix for HR-116 procedures were modified to sample the surface and ¼ inch depths. This change increased the number of operations to be performed on the samples by a factor of 5/3.

Evaluation of the near surface depth changes was also considered in the light of the changes in the structure of silica demonstrated by the Lentz data. This led to the formal partition of the silica analyzed into a coarse, fine, and soluble silica fraction and required the development of analytical techniques to determine these concentrations in the matrix samples. The coarse fraction represents the sand-sized residue of hydrochloric acid insoluble material and is interpreted to contain the quartz and feldspar particles originally added to the highway as sand when the concrete was mixed. The fine fraction, separated on the basis of size, represents material contributed by the cement which is insoluble in HCl and by the fine aggregate as minor amounts of fine quartz and feldspar material. Soluble silica represents primarily cement

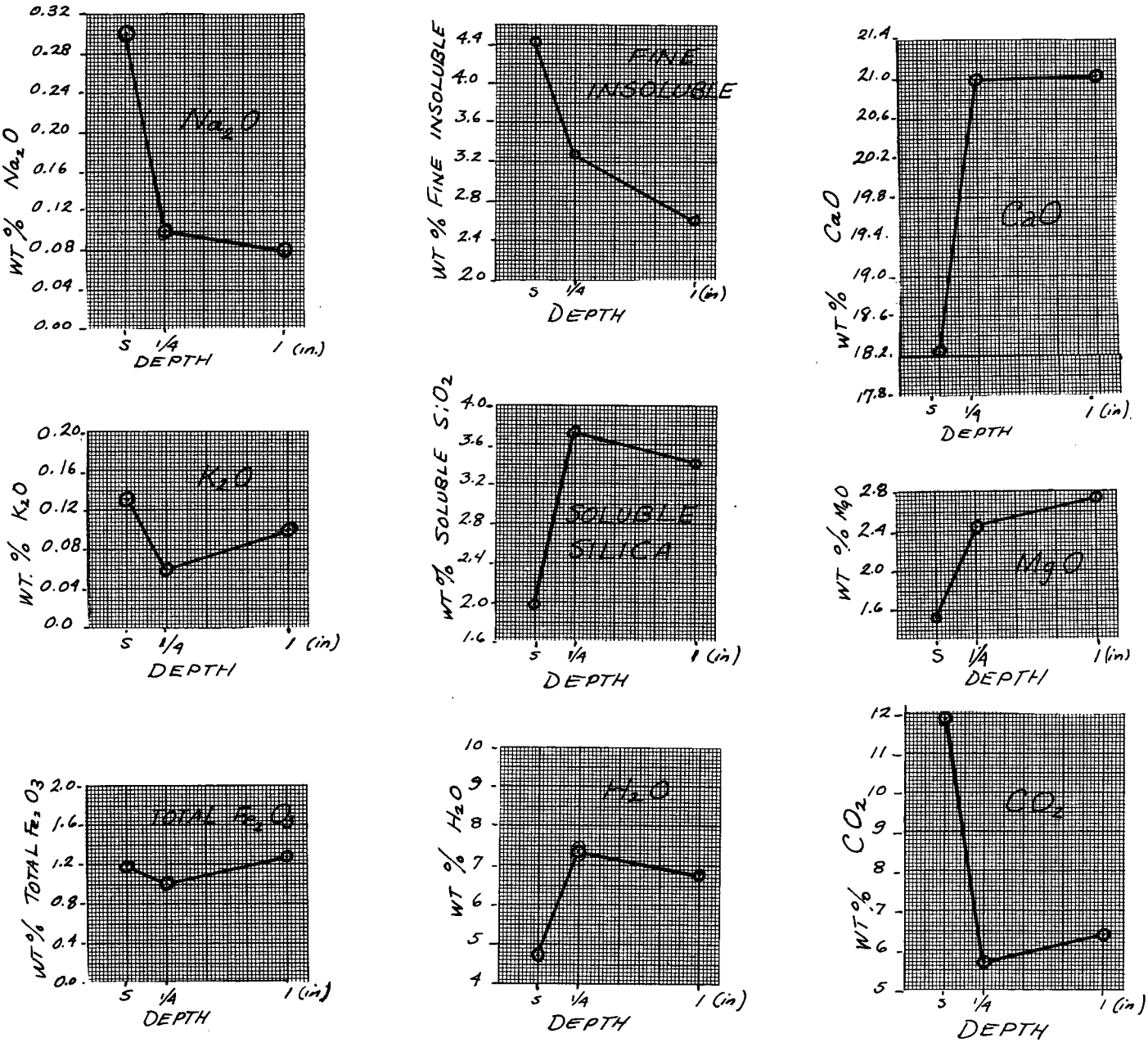

FIGURE 24. CHEMICAL CHANGES WITH DEPTH IN MATRIX OF 1952 OTIS AGGREGATE CONCRETE.

material present in a structure which is soluble in HCl and should correspond to the sum of the polysilicate, dimer and monomer forms of Lentz. Material balances through time and depth samples of HR-116 should detect relative changes in the silica concentration between sample fractions.

PETROGRAPHIC STUDY

Introduction

The systematic study of highway core samples taken under HR-116 is in progress and the state of the study is summarized below. Most of the time devoted to this aspect was spent developing the techniques for detecting differences between cores and in evaluating what differences were significant as discussed under preliminary data.

Program

In HR-116 a companion petrographic study was established to parallel the moisture, strength, and air content study which together with the bulk chemical study would contrast the behavior of Alden and Otis aggregate concrete systems. In addition several petrographic fences, consisting of a series of cores taken systematically across deteriorated areas near joints, were to be studied to contrast behavior of "damaged" slab edges with the "sound" center of slab samples which comprise the bulk of material tested. The number of cores selected for systematic petrographic study was as follows:

Center of slab - Otis aggregate concrete	14
Center of slab - Alden aggregate concrete	7
Petrographic fence - Otis aggregate concrete	35

The number of slices of core, representing the behavior of different depth materials which form the primary samples for the petrographic study are as follows:

Center of slab - Otis aggregate concrete	42
Center of slab - Alden aggregate concrete	21
Petrographic fence - Otis aggregate concrete	137

The systematic petrographic study is based on giving each slice a sample number which associates this slice with a particular depth in a particular core sample of the highway. After all the behavior of the slices has been noted the following questions are applicable to the evaluation of this study.

1. Otis aggregate concrete center of the slab samples

   a. How does the center of the slab change with time?

      1) Direct information:
      The comparison of 1966 slices with similar slices cored from the same slab in 1963 offered the best information on changes with time.

      2) Indirect information:
      Comparison of 1966 in the order of their service life may be used to detect consistent changes with time.

   b. How does the center of the slab change with depth?

      1) Since the slices are classified as to depth the above information is also applicable to depth structures.

2. Alden aggregate concrete center of the slab samples

   a. How does the center of the slab change with time?

   b. How does the change and the rate of change differ in Alden & Otis material?

3. Otis aggregate concrete fence samples

   a. What are the signs of deterioration in fence slices and how do they relate to the location of the joint surface?

   b. How do the fence slices differ from the expected behavior of the center of the slab?

The answers to the preceding questions should be interpreted in the light of the following symptoms of highway failure.

1. The brown appearance of aged highways.
2. D-cracking of highway slabs at joints.
3. Scaling of highway surfaces.
4. The blue appearance of natural fracture surfaces.
5. The progressive nature of distruction of material surrounding patches in highways.
6. Wear of highway surface.

The topics under which the comparisons of the petrographic behavior information are discussed are as follows:

Methods of Systematic Study

Results of Petrographic Study

- General Aspects
- Color Changes
- Coarse Aggregate Inner Rims
- Voids and Coatings
- Fractures
- Summary

Methods of Systematic Study

The flow sheet for petrographic analyses is shown in figure 25.

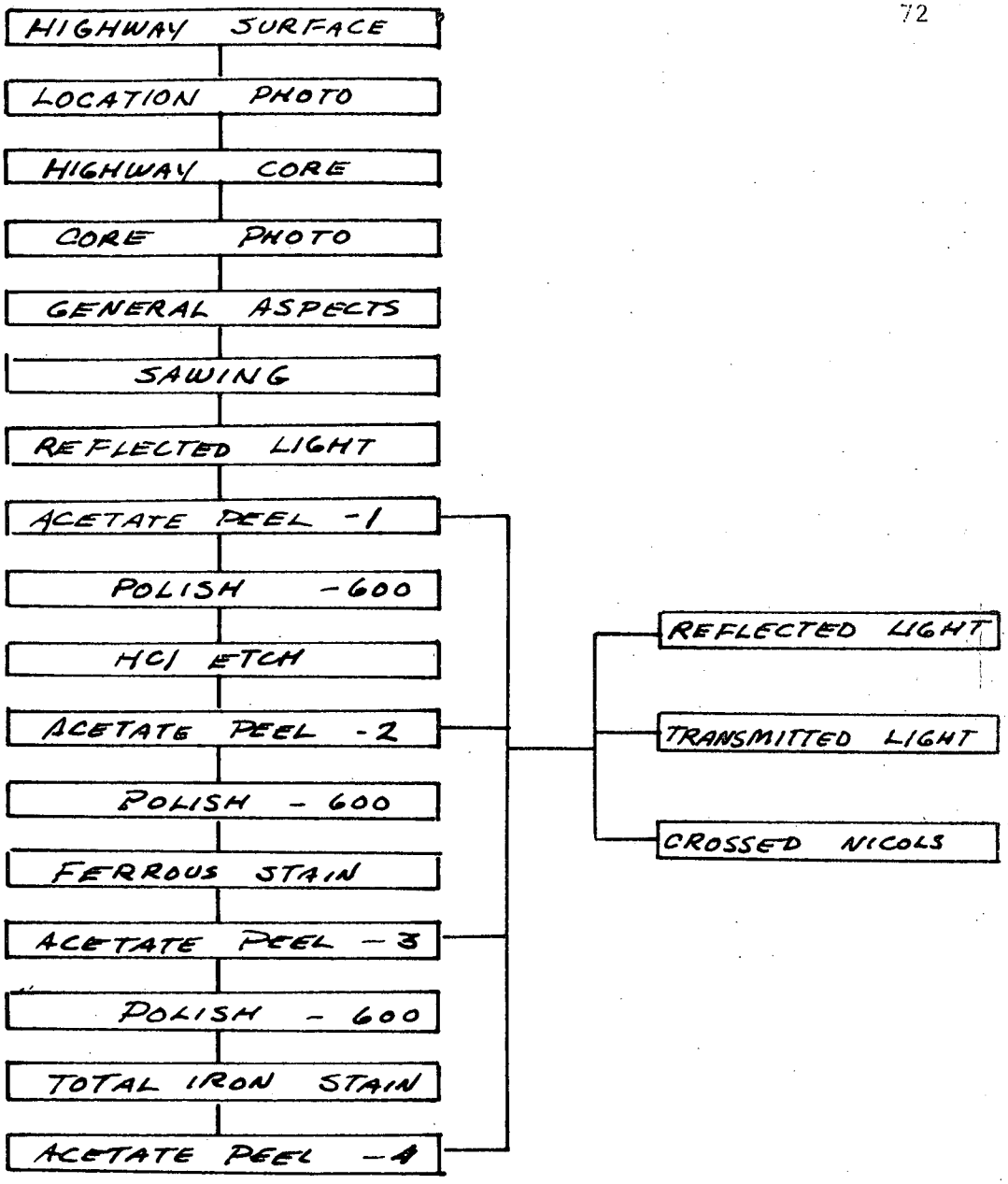

FIGURE 25. PETROGRAPHIC FLOW SHEET.

Acetate peel technique

A 0.003" thick clear acetate paper is bonded to a polished or sawed sample surface with acetone. In this process the acetate paper replicates the surface and has the following advantages which pertain to a petrographic study.

a. If the peel is left on the sample it preserves a wet sample surface. This permits evaluation of the color of the constituents and highlights the cracks and fracture surfaces. Such definition was formerly only possible after polishing through the finest grits which also fill the cracks with abrasive, or polished material.

b. If the peel is removed from the sample it may be mounted for observation under the microscope and it is suitable for study at magnification up to about 500X. The surface is preserved a material originally present in the cracks may be studied under transmitted or polarized light. Since the film has a biaxial negative character the normal birefringence of the film resembles quartz. Birefringence of trapped mineral fragments modifies the normal birefringence of the film and in this manner provides its mineral identity.

c. If the specimen is etched in HCl prior to bonding the acetate peel the etched surface is weakened sufficiently so the carbonate or cement fragments band more strongly to the peel than the sample surface. When the peel is removed a film of the acid soluble material is also removed so that the minerals in this acid soluble fraction of the surface may be studied under transmitted light. Comparisons of the peel morphology before and after etching is useful in distinguishing minor cracks from calcite veins.

d. Such peels are low-cost large-area samples which are easily indexed to the bulk material since the parent material is not destroyed in the process. Grinding of the surface will usually restore the sample surface to approximately the same features which were present before peeling. In studies of changes in mineral structure the peel technique may be used to locate the sensitive areas for which thin sections are desired and, after the thin section is obtained, serve as a map record of the surface sampled.

Acetate peel storing techniques

Surfaces may be stained with acid soluble dyes prior to the banding of the acetate peel. The dye etched surface is then removed with the peel. This technique has the advantage that different dyes may be applied to essentially the same surface so that dye distributions may be compared directly without the interference usually associated with repeated dying of the same surface.

Although acetate peel techniques were developed for the study of carbonate rocks, adaptation of this technique to the acid soluble fraction of the concrete matrix was a contribution of HR-116.

Results of the Petrographic Study

Tentative results which are consistent in the samples studied are presented under separate topics which reflect to level of the observations.

General aspects

1. The brown stain observed in highway surfaces is related to the source

of the coarse aggregate.

2. D-cracks in the surface are related to fractures and joints in the highway surface and to concentrations of certain coarse aggregates which appear as pop outs. D-cracks appear as filled cracks running between the pop outs.

3. Surface scale is related to the location of joints and fractures. Surface scale is also associated with the depth lighter colored matrix material at the highway surfaces. The depth of the scale is related to the type of coarse aggregate present, and perhaps to availability of moisture. It has a different character in the city and in the country. In the city it is much more rapid and little of the lighter colored matrix is observed at the surface. It appears that surface erosion occurs at a sufficient rate to prevent development of the surface zone at depth. In the country the loss of fine aggregate particles is much more gradual. From earlier studies, the general trend indicated that the matrix changes color and properties until bonds holding a particular fine aggregate piece on the surface are insufficient to keep it attached to the matrix. Removal of the piece exposed a fresh surface to further weathering action. However, additional observations indicate that there are other ways surface deterioration can occur.

For example, between the time the 1952 Otis core locations were marked and the time the material was cored, several large fragments were detached from the highway surface as shown in figure 26. Individual pieces as large as 3 x 5 inches were collected from the detached material. Such surface

A

B

C

FIGURE 26. SURFACE SCALING IN 1952 OTIS AGGREGATE CONCRETE.

scaling is related to availability of moisture, development of fracture patterns beneath the lighter material, and type of aggregate at the surface. These detached pieces occur as the removal of matrix material covering single coarse aggregate particles (pop outs) or as sheets of material covering concentrations of a particular type of highly fractured coarse aggregate.

4. Surface fracture patterns around joints are diverted away from the joint in a downward direction. Minor fractures are subparallel to the surface as the base of the light colored matrix area.

5. Fracture patterns also develop from the bottom of the slab adjacent to the joint zone and are diverted away from the joint in an upward direction. The intensity of fractures are related to the type of coarse aggregate present. Well-developed fracture patterns in the bottom of cores resulted in several short core samples.

6. In air-entrained cores the bottom fracture pattern appeared more extensively developed than the upper core fracture pattern. Not enough cores were observed to indicate whether this is true for any but the cores sampled. However, it is suspected that recent cores which are sealed underneath with polyethylene sheet are particularly susceptible to development of the bottom fracture pattern. For example, in the 1958 Otis fence series the bottom fracture sets were sufficiently developed to cause short cores at distances as much as three feet from the joint.

Color changes

In reflected light study of carbonate rocks one of the characteristic properties of a lithology is its color when viewed as a "wet" surface. The

use of acetate peel coverings on the surface of concrete samples permits comparison of the "wet" surfaces between samples. Since the coarse aggregate material came from Otis lithologies, the color of the coarse aggregate introduced into the highway should match the range of colors displayed by fresh and weathered rocks in the Otis Quarry. Colors which fall outside this range we assumed to result from interaction between the aggregate and its concrete environment. Some aggregates in Otis concrete show a progressive change from brown to yellow to white, depending on the length of time they have been in concrete and availability of moisture. Some aggregates change color as a unit in which the entire aggregate appears to fade. Other aggregate-types change color at the outer surface and are considered to form an inner rim. The rim progresses inward until the whole aggregate has the characteristics of the inner rim. Observations indicate that as the coarse aggregate becomes bleached with time, the matrix darkens from the colored material removed from the coarse aggregate and deposited in voids forming films on interfaces and fracture surfaces in the concrete. Certain Otis aggregate types were found to develop inner rims more rapidly in air entrained concrete. This is attributed to higher leaching rate in air entrained material.

Coarse aggregate inner rims

For a long time it has been known that inner rims have material properties which differ from the parent material. For example they are classified on the basis of HCl etching into negative rims, if they form peripheral depressions, and positive rims if they form elevated resistant peripheries. The relationship between these peripheral reaction zone features and concrete durability is not well understood. In our bending strength studies

of HR-86, inner rims were associated with the weak lithology. However, to most concrete petrographers they have remained features unrelated to concrete behavior. In this fence study it has been observed that fractures develop preferentially within the inner rim of certain Otis aggregate types. Upon fracture of the entire concrete core, the inner rim material separates to form the onion skin replicas of the original aggregate surface commonly associated with distressed concrete. Evidence supporting these observations are as follows:

1. Paragenesis - the sequence developed in susceptible aggregate type found in older concretes show unaltered aggregate, rims, cracks in rims, onion skinned fracture.
2. Chemical - use of the multiple acetate peel technique with ferrous and ferric iron determining dyes has demonstrated that a change from the ferrous to ferric iron state is associated with the change from parent to inner rim material in Otis aggregate concrete. Since the onion skin material is also associated with the ferric state it has the same properties as inner rim material. From this, it would appear that weakening of the aggregate to form the inner rim is a mechanism that accounts for onion skin type of failure. Since this rim formation is equated with both strong and weak aggregates a test similar to the bending strength study of HR-86 is needed to detect the weak rims among those aggregate types that form rims. If aggregate types that form weak rims were excluded from the original concrete material, then it would be expected that onion skin failures would be significantly reduced.

Voids and coatings

The voids and interfaces of the matrix and coarse aggregate are covered with a brown film. Calcium carbonate, iron colored isotropic gel, an isotropic white gel and fibrous bundles of the same morphology as tobermorite are observed in void areas. The fine aggregate appears to be attacked by the corrosive action of these films. This is especially true for iron material and calcium carbonate which are found in grain boundaries of quartz and feldspar fine aggregate. Almost complete disintegration of fine aggregate particles is associated with some zones in older concrete samples. These distressed fine aggregate particles form an onion skin surface in addition to grain boundary attack. In the transition zone between the lighter colored matrix and the darker matrix at the top core surface, the fine aggregate is attacked by the coating and possible volume change stresses to yield a zone of highly fractured fine aggregate. Even relatively large fine aggregate particles appear fractured in this zone. The carbonation of the matrix in this lighter colored zone is associated with a change from coarse to fine in the apparent grain size of the iron coating material and a thickening of this coating on the fine aggregate.

On the surface of the highway slab iron coating and the tobermorite morphology are associated with grooves in the fine aggregate and matrix which terminate in highly fractured fine aggregate particles. This appears to be one mechanism which acts to loosen the fine aggregate particles which are finally removed by traffic erosion.

Fractures

In Otis aggregate concrete the fractures in coarse aggregates have developed in CD-56 concrete with compressive strengths as low as 8430psi. Fractures are more evident in older concrete cores and in moist deteriorated zones near joints. Fractures appear to start in coarse aggregates near sources of moisture such as large voids. In aggregates which form inner rims, fractures commonly occur in inner rims and parallel the inner rim-unreacted aggregate boundary. Stronger cores also display cracks which start around the larger voids. This evidence supports the conclusions of the moisture study that the matrix of high strength cores (high % Saturation) are susceptible to fractures.

Summary

The overall pattern of distressed Otis Aggregate concrete appears to be as follows:

1. Increase in strength of the concrete material with time.

2. Leaching of iron material from the aggregate and deposition of this material within the matrix.

3. The matrix becomes stronger than some aggregate types.

4. Failure of the aggregates by progressive or fatigue type fracture within the weakest zone.

5. Iron material is removed at a more rapid rate along the increased surface of the fractured zones. Coatings serve to keep fractures open.

6. Fracture of the high strength concrete around large voids (possible freeze and thaw behavior).

7. Interconnection of the major fractures with the coarse aggregate and matrix.

8. Failure of the core along a fracture plane associated with onion skins of coarse and fine aggregate particles.

CHEMICAL CHANGES WITH DEPTH AND IN CENTER OF CORES

The preliminary investigation on the Otis aggregate concrete CD-52 sample at surface, ¼ and 1 inch depths indicated that chemical and mineralogical changes occurred at and near the surface of the highway concrete. As a result, a systematic sampling and chemical study was undertaken on the 1966 highway core samples to investigate these changes. A 1/8 inch thick slice was taken at the surface and ¼ inch depths on two of the three cores designated for chemical study. Then two 1/8 inch slices were taken at the 1, 3, and 5 inch depth on all three cores as shown in figure 1. The uppermost one inch of the one core was saved for petrographic study. Although the 1963 chemical data showed that the 1, 3, and 5 inch depths samples were in essence a measurement of the same material, the 1, 3, and 5 inch layers were again sampled to see if changes with time are reproducible. These slices were carefully separated into matrix, aggregate and waste portions. The matrix material consisted of the hydrated cement compounds and the fine aggregate, the aggregate consisted of the coarse carbonate aggregate and the waste consisted of the remaining material that was neither wholly matrix nor aggregate. The matrix samples from each core depth were blended into one sample for each depth respectively and dried at 110°C prior to chemical analysis.

Figure 27 presents a flow sheet outlining the procedure for a systematic analysis of the various matrix samples. The data which reflect the work status as of present time is given in Table IX. The numbers reported for

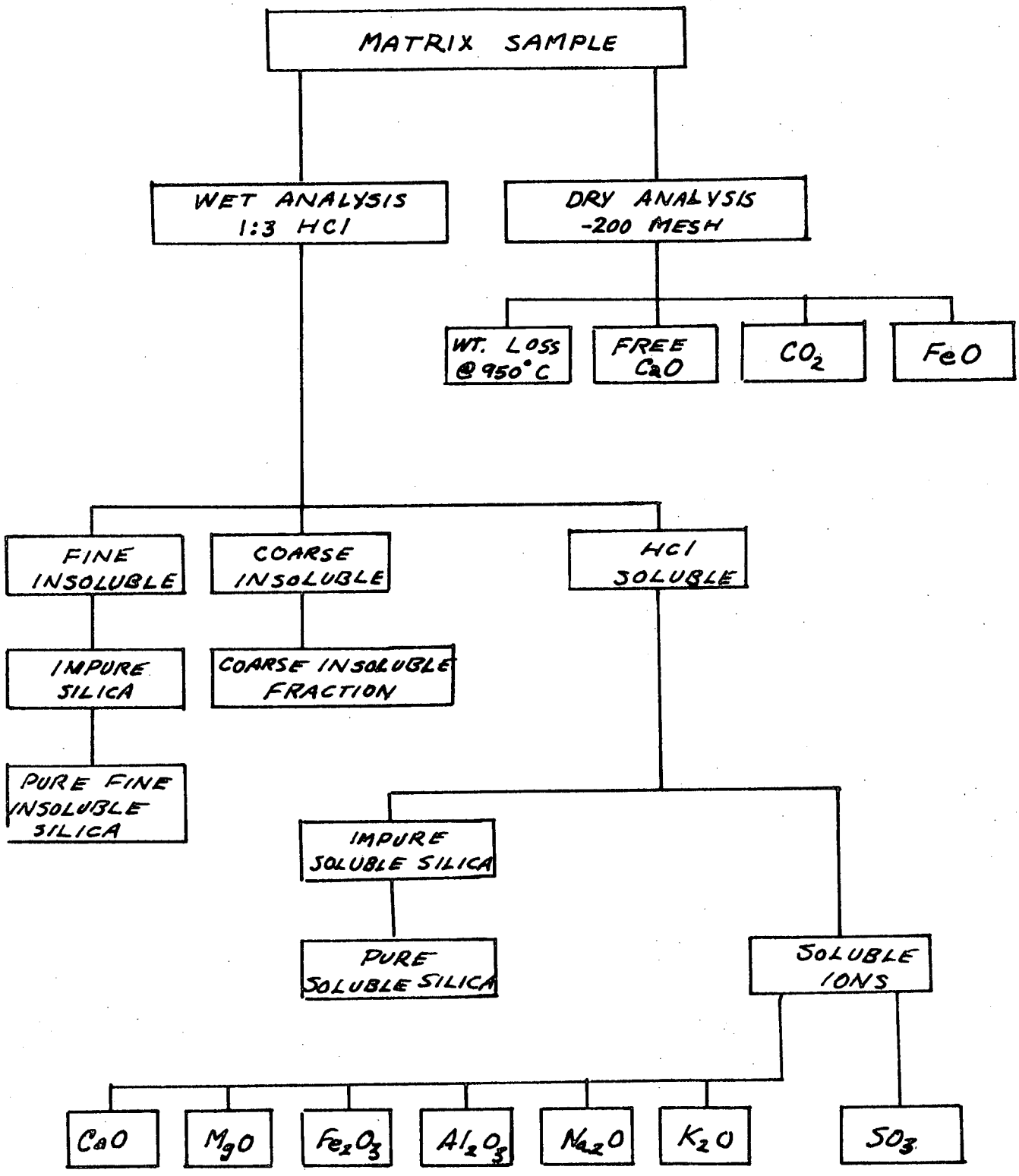

FIGURE 27. CHEMICAL ANALYSIS FLOW SHEET FOR HR 116 .

TABLE IX Chemical analysis data of matrix material taken from 1966 cores at surface, 1/4, 1, 3, and 5 inch depths reported on total weight percent basis.
Data below only for Otis aggregate concretes

CORE IDENTIFICATION	DEPTH	① Coarse Insoluble Fraction	② Fine Insoluble (pure SiO_2)	③ Pure Soluble Silica	④ % Soluble Sample	⑤ Wt. % Total CaO	⑥ Wt. % MgO	⑦ Wt. % Total Fe_2O_3	⑧ Wt. % Al_2O_3	⑨ Wt. % Na_2O	⑩ Wt. % K_2O	⑪ % Wt. Loss @ 950° C	⑫ % Fixed H_2O	⑬ Wt. % CO_2	⑭ Wt. % Free CaO
CD-66-61-150	S	30.11	30.77	0.81	35.96	16.36	2.10	0.92		0.56	0.28	13.93	2.55	11.38	0.47
CD-66-61-150	1/4	31.97	27.40	2.48	35.65	18.31	1.97	1.38		0.13	0.11	9.34	6.06	3.28	4.91
CD-66-61-150	1	30.61	29.64	3.14	34.16	18.44	2.16	1.51		0.08	0.11	9.54	6.54	3.01	4.35
CD-66-61-150	3	29.03	30.05	2.64	36.17	18.87	2.63	1.38		0.08	0.10	9.33	5.62	3.71	4.38
CD-66-61-150	5	27.13	30.23	3.32	34.98	18.73	2.95	1.57		0.08	0.11	9.70	6.05	3.65	4.55
CD-66-58-150	S	29.89				19.71	1.37	0.82		0.46	0.15	14.18	4.05	10.13	0.84
CD-66-58-150	1/4	35.85				19.45	1.63	0.81		0.10	0.06	9.24	4.05	5.19	3.50
CD-66-58-150	1	35.83				19.74	1.57	0.94		0.09	0.08	9.09	6.58	2.51	4.29
CD-66-58-150	3														
CD-66-58-150	5														
CD-66-57-W	S	29.29				17.21	1.67	0.92		0.09	0.14	14.90	3.22	11.68	0.13
CD-66-57-W	1/4	40.75				16.64	1.95	0.85		0.09	0.10	9.92	4.34	5.58	1.99
CD-66-57-W	1	37.98				17.94	2.43	0.90		0.07	0.08	8.66	5.07	3.59	3.90
CD-66-57-W	3														
CD-66-57-W	5														
CD-66-56-218	S	26.22	30.69			18.14	2.41	0.87		0.49	0.18	14.47	2.86	11.61	0.30
CD-66-56-218	1/4	34.93	20.10			18.13	1.89	0.91		0.15	0.07	9.24	4.82	4.42	2.77
CD-66-56-218	1	36.42	20.84			18.44	2.69	1.00		0.08	0.10	9.42	5.01	4.41	3.76
CD-66-56-218	3	35.63	23.11			18.70	2.45	1.05		0.08	0.09	8.77	4.78	3.99	3.62
CD-66-56-218	5	33.66	25.29			18.19	2.84	1.07		0.07	0.08	8.16	3.97	4.19	3.75
CD-66-52-1	S	30.93	27.62	1.38	35.60	17.86	2.34	0.97		0.54	0.18	14.33	2.84	11.41	0.27
CD-66-52-1	1/4	38.71	20.50	4.64	34.08	18.33	2.16	1.06		0.20	0.09	10.14	6.21	3.93	3.18
CD-66-52-1	1	41.04	18.66	5.66	32.35	18.48	2.35	1.06		0.08	0.09	8.40	5.37	3.03	4.07
CD-66-52-1	3	42.16	17.32	5.65	32.78	18.69	2.15	1.21		0.08	0.11	8.23	5.39	2.84	4.16
CD-66-52-1	5	45.09	16.73	5.18	30.94	17.65	2.19	1.17		0.08	0.10	8.63	5.35	3.28	4.02
CD-66-50-151	S	27.87	27.26	3.96	37.68	20.57	2.90	1.23		0.19	0.09	11.10	3.37	7.73	3.35
CD-66-50-151	1/4	34.32	19.36	5.16	38.88	22.09	2.45	1.31		0.03	0.07	11.18	4.13	7.05	4.15
CD-66-50-151	1	36.07	17.92	5.44	38.58	21.49	2.69	1.45		0.09	0.12	11.28	5.31	5.97	4.26
CD-66-50-151	3	35.14	18.28	5.25	39.42	22.19	2.68	1.41		0.08	0.11	10.73	4.92	5.81	4.11
CD-66-50-151	5	32.66	20.92	4.92	39.00	21.74	3.11	1.28		0.08	0.10	10.43	5.57	4.86	4.16
CD-66-48-151	S	37.27	14.54	7.24	38.70	20.51	2.86	1.14		0.22	0.09	13.06	5.22	7.84	2.60
CD-66-48-151	1/4	42.12	10.67	6.33	38.55	21.54	2.84	0.43		0.14	0.08	12.64	6.71	5.93	4.11
CD-66-48-151	1	39.72	11.88	6.97	39.11	21.99	2.96	1.28		0.09	0.13	11.50	6.78	4.72	4.49
CD-66-48-151	3	42.98	9.21	6.44	39.57	20.23	2.39	1.22		0.09	0.12	12.53	7.14	5.39	4.73
CD-66-48-151	5	40.07	12.29	7.56	38.27	21.30	2.72	1.36		0.08	0.11	11.45	6.74	4.98	4.44

* Identification Code: CD - Otis aggregate
First pair of digits = year highway sampled
Second pair of digits = year highway poured
Last pair of digits = highway designation

** % Fixed H_2O: % Wt. Loss @ 950 - % CO_2

*** % Free CaO: % $Ca(OH)_2$ as CaO

the surface and ½ inch samples are the result of a single determination because of a limited quantity of sample. The numerical values shown for the 1, 3, and 5 inch depths are the average of duplicate determinations. Duplicate determinations agreed within 3% of the value reported and commonly averaged 1%. This is considered very good agreement for the heterogenity expected of the chemical system sampled.

The partitioning of the silica into the various categories is used to determine the possible chemical changes taking place within the silica system. Soluble silica is defined as that material which is in a cation form in the HCl solution. The primary source of it is from the cement hydrate compounds and assumed here to be entirely from this source. The coarse insoluble fraction represents the bulk of the fine aggregate material. The fine insoluble fraction is the remaining portion of the fine aggregate plus the HCl insoluble silica that may be present within the sample material.

The calcium partition consists of the total calcium determined by EDTA Titration, the $Ca(OH)_2$ reported as CaO determined by the isobutyl alcohol-ethyl acetoacetate extraction of Franke as modified by Brunauer, Copeland, Pressler & Kantro (1961). The CaO associated with $CaCO_3$ is calculated from the CO_2 content. The CaO in theCSH (hydrated calcium silicate compounds in the cement) is defined as follows:

$$Ca(CSH) = (\text{total CaO}) - (\text{CaO in } CaCO_3) - (\text{free CaO})$$

The water content of the material can be subdivided in the following three categories:

Fixed H_2O = (Wt. Loss @ 950°C) - (CO_2)

Hydrolysis H_2O = Amount of water in $Ca(OH)_2$

Hydration H_2O = (Fixed H_2O) - (Hydrolysis H_2O)

From the three partitions briefly explained above, an estimate of the hydrated cement compounds can be computed.

Figures 28, 29, 30, and 31, giving the chemical changes with depth for CD-66-52-1 (1952 Otis aggregate concrete), are presented to give a graphic representation of the chemical changes observed at the surface of this concrete. Upon consideration of the various depth versus concentration curves, it can be shown that the 1, 3, and 5 inch concentrations vary only a minor amount with depth. Therefore, the average value for the 1, 3, and 5 inch layers is assumed to be a reproducible value characteristic of a given center of slab highway material.

Table X summarizes the changes that are shown in figures 28,29,30, and 31.

Table X: SURFACE CHEMICAL CHANGES

Increasing at Surface	Decreasing at Surface
1. Fine insoluble silica	1. Fixed H_2O
2. CO_2	2. Hydration H_2O
3. Weight Loss @ 950°C	3. Hydrolysis H_2O
4. Equivalent Na_2O	4. Soluble Silica
5. Ratio: $\frac{H_2O \text{ (Hydration)}}{SiO_2 \text{ (Soluble)}}$	5. Coarse Insoluble Fraction
6. Ratio: $\frac{H_2O \text{ (Hydration)}}{CaO \text{ (CSH Compounds)}}$	6. Total CaO
	7. Free CaO
	8. CaO (CSH Compounds)

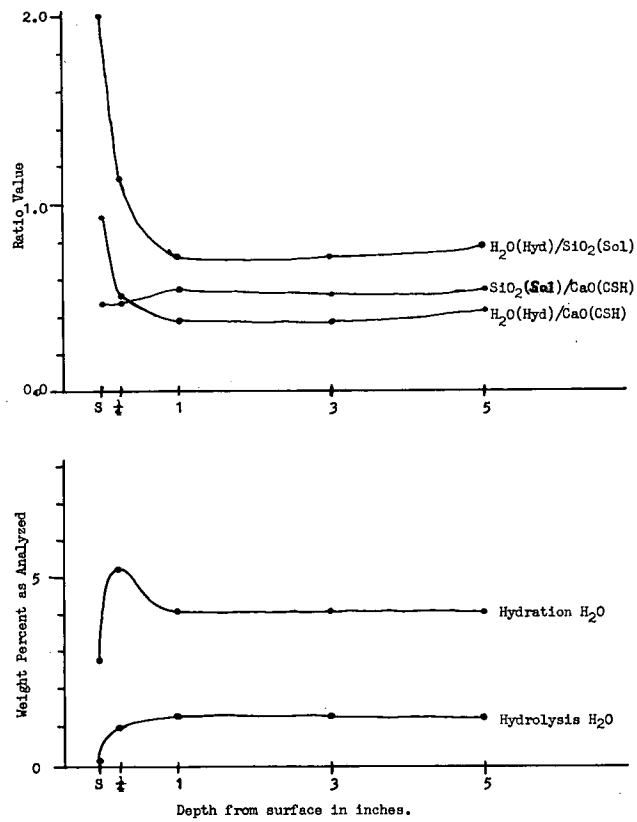

FIGURE 28 Chemical changes with depth, CD-66-52-1.

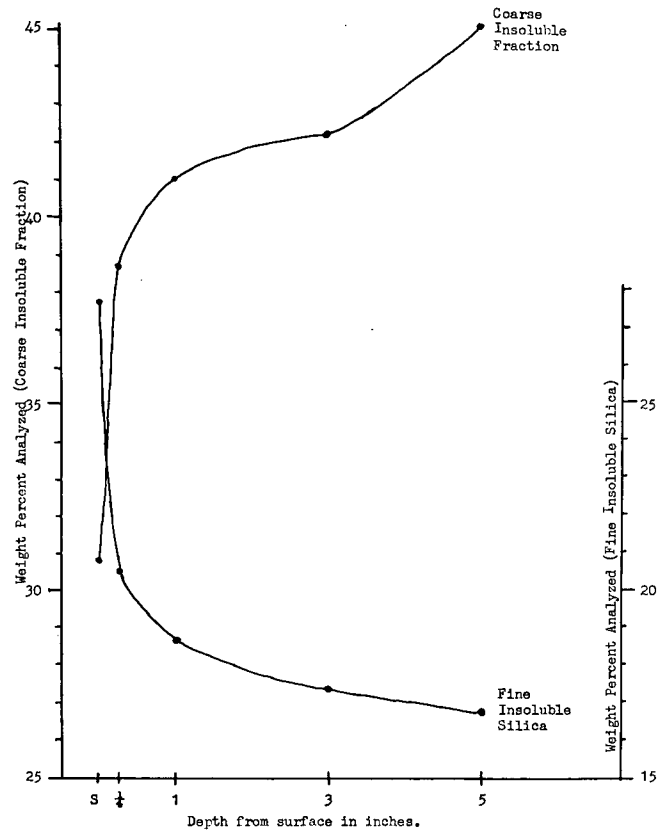

FIGURE 29 Chemical changes with depth, CD-66-52-1.

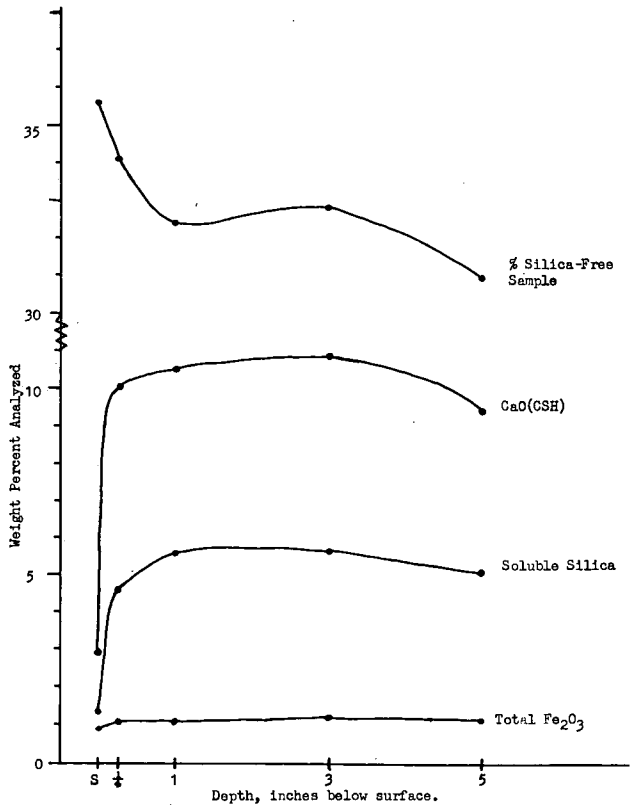

FIGURE 30 Chemical changes with depth, CD-66-52-1.

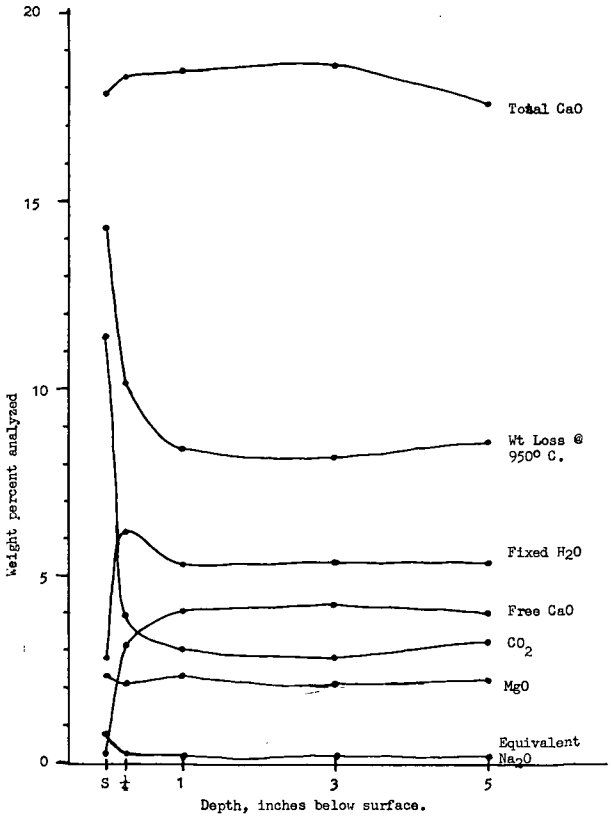

FIGURE 31 Chemical changes with depth, CD-66-52-1.

Tentative conclusions and interrelationships drawn from the above data are as follows:

1. The biggest change noted is the 3-fold increase of the CO_2 content at the surface. This change is also correlated to the large decrease in free CaO content. Therefore the large CO_2 content at the surface is in the form of $CaCO_3$ and results from the CO_2 attack on the $Ca(OH)_2$ and later on the CSH compounds. Bogue (1956) states that the CO_2 content of concretes may be entirely attributed to $CaCO_3$. This $CaCO_3$ - rich zone at the surface will be referred to as the carbonate zone.

2. The decrease in amounts of soluble silica and CaO (CSH) (CaO from hydrated cement compounds) may be attributed to the CO_2 attack on the hydrated cement compounds. The CO_2 attack on these compounds would immediately follow the removal of the $Ca(OH)_2$ from the system as $CaCO_3$. The decrease in soluble silica and CaO(CSH) lends support to this idea. Assuming the soluble silica and CaO(CSH) results only from acid attack of hydrated cement compounds (CSH compounds), the CO_2 attack should reduce the relative abundance of the CSH compounds yielding relatively less soluble silica and CaO(CSH). Another fact that the CSH compounds are attacked and completely broken down is that the soluble silica to CaO(CSH) ratio is essentially constant for throughout the inner core.

3. The increase in fine insoluble silica is partially attributed to the breakdown of the hydrated cement compounds by CO_2. Silica in the CSH compounds probably is rendered acid insoluble as a $SiO_2 \cdot H_2O$ compound.

The other source of fine insoluble silica is the fracturing of the fine aggregate that was petrographically observed in and at the bottom edge of the surface zone. This fracturing of the fine aggregate is shown by a decrease of the coarse insoluble fraction, or the fine aggregate portion of the concrete.

4. Figure 32 presents the alkali changes with depth for different ages of Otis aggregate concrete at the surface, ¼, 1, 3, and 5 inch depths. The interior of the concretes all show about the same equilibrium concentration well below the original equivalent Na_2O content in the raw cement. These data verify our original HR-86 data that the mobile alkali moves the concrete. However, the surface and ¼ inch depths show high alkali concentration where the alkali had migrated as a result of wetting and drying cycles. The CD-66-50-151 and CD-66-48-151 samples occur within city limits and have a much lower surficial alkali concentration possibly due to traffic erosion. These alkali data indicate that a high pH environment exists at the surface which can induce secondary reactions capable of changing the surficial properties of concrete.

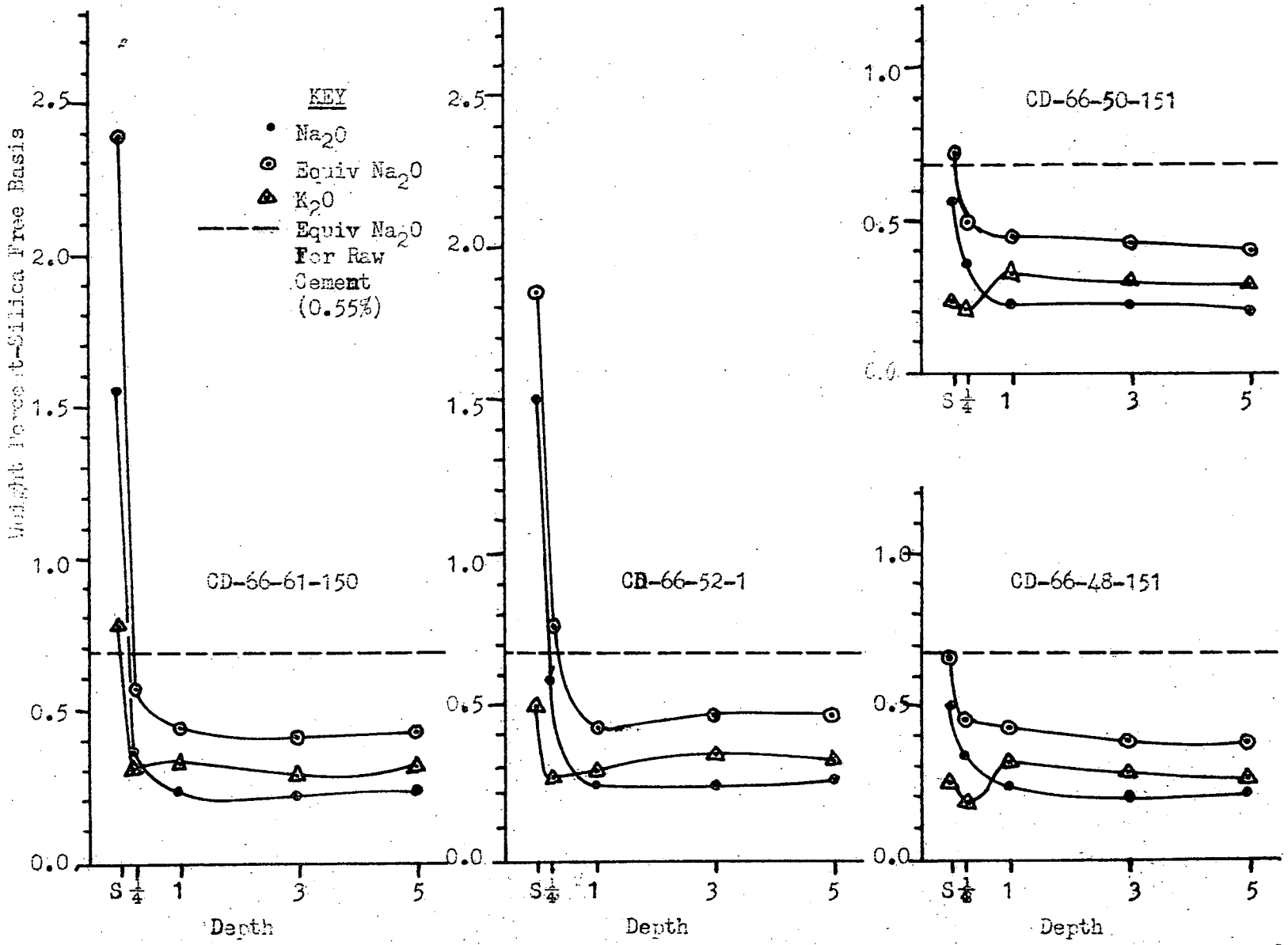

FIGURE 32. Alkali changes with depth, on a silica free basis.

SUMMARY AND CONCLUSIONS

General Statement

Several investigations have been described in this report which are all interrelated aspects of concrete behavior. Within this concrete-centered approach, it soon becomes evident that a strong dependence on source of cement and/or aggregate exists when any aspect of concrete aging is considered. The reverse approach, aggregate-centered studies based on service records, has long been recognized and accepted and has served as the essential basis for many research projects, few of which have given any direct answers for mechanisms by which aggregates cause distress in concrete. The major contribution of this approach is that it states the problem and focuses attention on the role of aggregates. The concrete-centered approach exemplified by our concrete aging studies has, on the other hand, brought out and served as a better basis for understanding mechanisms of how aggregates are related to concrete service since it focuses attention on the basic ingredients of the concrete system which are coarse aggregate, fine aggregate, cement, water, and time. Current research is showing that all of them are interrelated to overall concrete performance which, in turn, proved the initial assumption of performance must be dependence on the ingredients. This generalization which served as the basic premise in our original research on concrete aging, has now been shown to be a reality in HR-116 because of the strong dependence of concrete performance on the source of cement or aggregate. This interdependence in turn will do much toward achieving a greater level of predictability for evaluating performance of aggregate and cements

for concretes from which realistic specifications can be set.

This is a major conclusion drawn from all aspects of our research to date. It is also evident that this basic relationship as well as the other conclusions which will follow, are the product of a concentrated study in ever greater detail on two systems of concrete made from aggregates with different and contrasting service (Otis and Alden) history. By developing new techniques of study on two basic systems of concrete, it has been possible to make more different kinds of observations which have provided for more meaningful understanding. An example of this approach is the collection of a considerable amount of data from many types of observations on a basic set of samples. This permits pyramiding information which allows one to check interrelationships of many variables; this is especially important in problems relating to mechanisms by which processes during concrete aging occur. After a mechanism has been determined, it then becomes feasible to make a few special tests or observations on many systems to check the range and applicability of a given type of test.

Our research, then, in HR-116 has consisted of taking an approach in which many levels and types of observations are made on two systems of concrete. An example of this would be the compressive strength studies. If we were interested in testing the relationship of compressive strengths with time, a series of compressive strength tests could have been run on the Alden, Otis, Dubuque, and Iowa City aggregate concretes of different ages. Inconclusive data would have resulted from this approach which has been tried before by others in different systems. This is because there is so much variation in just the cement-dependent properties alone that any relationship would have been difficult to detect. If, however, com-

pressive strength is checked in addition to other dependent variables (such as water, air, cement source, type of aggregate and age) the true role of strength could then be evaluated. This has been the basic approach which has been followed in our research and is mentioned in our conclusions because it emphasizes the importance of studies in depth.

The specific conclusions drawn from the several aspects reviewed in this report will be summarized, and then the practical aspects of these conclusions will be discussed. Suggestions for future research will conclude the report.

Specific Conclusions

The study concerning phase changes in cement materials by Lentz indicated that the CSH compounds change with time. The ratio and type of change from monomer and dimer to higher polysilicate forms is dependent on the source of cement and aggregate. It indicates also that cements differ with regard to their initial contents of monomer, dimer and polysilicate material and this variation may be related to their performance. The cementing materials in Alden cores are still hydrating into dimer forms. The cementing materials in Otis concretes are converting into higher polysilicate forms and are weakening.

The study of the relationship of compressive strength to air and water content of the concrete produced data that compressive strength of concrete is related to the percent saturation which in turn is dependent on changes which are occurring in the pore structure of concrete. Pore structure changes are dependent on the contribution from the coarse aggregate. The data show that no matter how much air is designed into a

concrete, the unfilled voids remain between 1 to 2%.

Petrographic fence studies extend further the observations initially made in Elwell's study of Otis concretes. Iron gel occurs in all surfaces, cracks and voids in our deterioration zones. Iron gel is controlled by cracks and boundaries in the system including fine as well as coarse aggregates. The removal of iron gel through channels in negative rim zones definitely is related to the weakening of these zones. Upon migration of gel into the matrix it appears to have a disruptive effect on fine aggregate, especially at the matrix - fine aggregate contacts. It is difficult to say whether the freezing or the iron gel causes or contributes to disruptive effects in rim and matrix areas. Sequential data obtained from aging and fence studies indicate that both appear to create a cummulative effect; freezing may cause cracks and gels help keep the crack open, thereby aiding crack migration.

Vertical chemical changes are present in nearly all concretes. Mobile matter migrates up and is concentrated at the surface because of capillary and drying action all concrete slabs are subject to. This process causes a differentiation of materials in the concrete system depending on their relative mobility. The surface concentrations are slowly removed by flushing action of rain water and traffic erosion. Sodium and potassium are concentrated on the uppermost layer leaving the remaining concrete with a much lower alkali concentration. This surficial alkali concentration raises the pH locally. Evidence is also present that carbonation is increased at the surface, CSH compounds break down, and fine aggregates are disrupted in this zone. The net result is that the surface layer is of different composition, hence possesses different properties than the rest of the system. The net result such as spalling, in turn depends on rate

of surface differentiation relative to surface lowering by erosion.

In combining data from all aspects of our study it is apparent that the changes related to deterioration are related to a series of progressive physical and chemical changes in concrete. Presented below as the final summary is a tentative model derived from integrated data for the deterioration of Otis aggregate concrete.

As air entrainment voids become progressively filled with reaction products derived from coarse aggregates, the mass of the matrix increases favoring an increase in strength. The filling process may be depleting voids faster than water is lost from air entrainment sized pores. This causes a net increase in the percent saturation and if this continues to a point below the margin of air needed for freezing protection, damage can occur. Observation of fractures following weakened rim zones, gel coated interfaces and the fact that they either originate from or connect large voids, shows the general way deterioration is preferentially controlled by features in turn affected or preconditioned by other physical and chemical processes. The chemical data and knowledge of the structural forms of our CSH compounds fits into the above picture when related to compressive strength data. Knowledge that our poor service record concrete (Otis) has higher compressive strength than concretes with good service records indicates that the matrix has increased in strength beyond the strength of the aggregates. This is also related either to the initial CSH content of the cement or the faster rates at which hydration occur. Alden concretes show lower strength, lower initial CSH content, evidence that CSH compounds are still forming and a good service record. These relationships all indicate the overall path and nature of the aging and deterioration process and how it can be effected by reaction processes

of aggregates with cementing materials in our concrete environment.

Practical Aspects

The petrographic study of the Otis aggregate in concrete demonstrated a way of identifying lithologies into weak and strong types. It was found that the weak lithologies (most of them) exist in the lower half of the section exposed in the Otis quarry. It appears feasible that some tests be made which contrast the performance in concretes of rock from the upper and lower ledges.

The compressive strength, air, and water studies demonstrated a systematic way of approaching of determining the conditioning of concrete, and provide a way of establishing criteria for concrete condition. Such tests, if systematically employed and tested, may eventually provide means of having criteria upon which we can maintain our highways, and possibly modify some of our current practice with regard to design, placing of concrete, material specification and tests, and maintenance.

Future Research

The direction of future research, although similar to what was described in this report, will require more detailed studies in the following areas:

(1). More detailed petrographic study of aged and deteriorated concrete at higher magnification with the electron microscope to investigate the nature of coatings in voids and fractures.

(2). Further studies on relationship of compressive strength to air and moisture contents of concretes.

(3). Chemical studies of concrete which are integrated with the petrographic study described in (1) above.

APPENDIX I

AIR ENTRAINMENT STUDY

Data for Air, Moisture, and Strength from ISHC Testing Lab

By drying before the 48 hour soak, the air content obtained represents total entrained air. This includes those pores in the smaller sizes that have original water in them that has never escaped. This is ASTM procedure run on "B" and "C" designated cores.

By not drying the cores, the air content represents the "effective" entrained air. That is, the pores that are actually filled with air. Whether or not these air filled pores are actually in the effective size range cannot be determined with the high pressure air meter. This procedure was run on "A" designated cores.

Specifications	beginning	with	1952	required	3 - 5% air
"	"	"	1956	"	4 - 6% "
"	"	"	1960	"	5 - 7% "

NOTE ON ERRORS IN DATA

*CD-66-54-220 was not an Otis aggregate concrete. It is considered to be Iowa City stone and its data is extraneous.

**CD-66-51-W and CD-66-57 are not in chronological sequence; their positions are reversed in the table received from the Highway Commission.

***A-66-57-20 was found to be a gravel aggregate concrete. These data are extraneous.

TABLE XI -- STRENGTH DATA OF 1963 CORES (HR86)

Core Code	Average Compressive Strength	Age at Test Time	Cement Source
*A-30	7805	34	Hawkeye
A-57	8001	32	Penn Dixie
A-60	7462	27	Penn Dixie
**CD-38	8627	25	Dewey
CD-41	10,000	22	Penn Dixie
CD-46	9698	17	Dewey
CD-52	8230	11	Dewey
CD-56	8430	7	Dewey
CD-58	8701	5	Penn Dixie
CD-61	7136	2	Dewey

*A = Alden aggregate concrete; digits represent highway number
**CD = Otis aggregate concrete; digits represent year of paving

	Core Identification	Station	Length	Weight As Received	Weight After 48 Hr. Soak	% Air	Weight After 2 Hr. Soak	Weight After Drying Period	Weight After 48 Hr. Soak	Weight In Water	% Air
A-1	CD-66-38-38	208+20	6.50	3209		0.9	3238	3055	3220	1886	2.4
A-2	CD-66-41-1	666	7.75	3944		0.3	3970	3780	3956	2335	1.8
A-3	CD-66-46-1	840	9.00	4539		0.7	4570	4336	4550	2693	2.7
A-4	CD-66-48		8.90	4388		0.2	4418	4178	4400	2565	2.6
A-5	CD-66-48-3	204	7.00	3480		2.0	3510	3325	3488	2040	4.4
A-6	CD-66-48-84	161+10	9.00	4380		1.7	4425	4130	4390	2530	2.6
A-7	CD-66-48-151	43	7.40	3535		2.6	3595	3370	3550	2035	4.9
A-8	CD-66-50-151	43	7.80	3818		0.6	3845	3650	3824	2212	3.8
** A-9	CD-66-57 Co. W	16 +	5.50	2679		1.3	2715	2558	2695	1557	4.0
A-10	CD-66-52-1	227+80	8.50	4068		3.1	4115	3894	4080	2335	5.6
* A-11	CD-66-54-220	259	8.40	4016		2.6	4070	3848	4040	2320	3.8
A-12	CD-66-56-218	250+75	9.60	4595		2.0	4660	4385	4610	2642	5.2
*** A-13	CD-66-51-COW		7.00	3424		1.4	3465	3278	3435	2003	3.3
A-14	CD-58-150	59	10.00	4920		1.0	4980	4685	4948	2848	3.7
A-15	CD-66-61-150	213	10.00	4672		1.6	4740	4424	4695	2663	5.3

	Core Identification	Station	Length	Weight As Received	Weight After 48 Hr. Soak	% Air	Weight After 2 Hr. Soak	Weight After Drying Period 72 Hrs.	Weight After 48 Hr. Soak	Weight In Water	% Air
B-1	CD-66-38-38	208+20	6.4					2770	2915	1715	1.7
B-2	CD-66-41-1	666	7.7					3380	3540	2085	1.7
B-3	CD-66-46-1	840	9.5								
B-4	CD-66-48		9.1					3785	3963	2328	1.9
B-5	CD-66-48-3	204	7.1					3118	3268	1886	3.6
B-6	CD-66-48-84	161+10	9.3					3560	3774	2183	2.0
B-7	CD-66-48-151	43	7.4					3065	3235	1860	4.6
B-8	CD-66-50-151	43	7.9					3405	3570	2072	3.2
B-9	CD-66-57-COW		5.9					2385	2513	1450	3.6
B-10	CD-66-52-1	227+80	8.6					3545	3708	2140	4.4
B-11	CD-66-54-220	259	8.3					3425	3606	2059	3.9
B-12	CD-66-56-218	250+75	9.3					3565	3741	2158	4.0
B-13	CD-66-51-COW	16+	6.6								
B-14	CD-66-58-150	59	10.0					3570	3782	2188	2.1
B-15	CD-66-61-150	213	10.0					3412	3630	2057	4.4

	Core Identification	Station	Length	Weight As Received	Weight After 48 Hr. Soak	% Air	Weight After 2 Hr. Soak	Weight After Drying Period	Weight After 48 Hr. Soak	Weight In Water	% Air
C-1	CD-66-38-38	208+20	6.9					3015	3180	1863	1.4
C-2	CD-66-41-1	666	7.4								
C-3	CD-66-46-1	840	9.3					3630	3810	2225	2.2
C-4	CD-66-48		8.7					3670	3843	2250	2.2
C-5	CD-66-48-3	204	6.8					2885	3018	1747	4.1
C-6	CD-66-48-84	161+10	8.9					3660	3870	2243	2.2
C-7	CD-66-48-151	43	7.0					3155	3330	1955	4.0
C-8	CD-66-50-151	43	7.9					3415	3573	2078	3.2
C-9	CD-66-57-COW		5.8					2430	2565	1473	3.9
C-10	CD-66-52-1	227+80	8.4					3700	3883	2225	5.2
C-11	CD-66-54-220	259	8.1					3455	3633	2083	3.5
C-12	CD-66-56-218	250+75	9.3					3550	3700	2138	4.2
C-13	CD-66-51-COW	16+	7.0					3150	3314	1937	2.9
C-14	CD-66-58-150	59	10.5					3425	3620	2095	2.2
C-15	CD-66-61-150	213	10.2					3414	3640	2060	4.4

	Core Identification	Station	Uncut Length	Weight As Received	Weight After 48 Hr. Soak	% Air	Weight After 2 Hr. Soak	Weight After Drying Period	Weight After 48 Hr. Soak	Weight In Water	% Air
A-1	A66-65-65	12	10.15	4687		1.6	4730	4425	4692	2624	6.9
*** A-2	A66-57-20	168	9.65	4240		5.9	4365	4017	4275	2367	7.8
A-3	A66-51-383	22	7.45	3503		1.2	3535	3317	3502	2040	2.4
A-4	A66-51-6	1923 & 75	9.95	4828		2.0	4882	4585	4837	2805	3.0
A-5	A66-50-14	765 & 80	8.00	3863		1.8	3904	3675	3876	2242	2.8
A-6	A66-41-14	37	7.50	3557		1.5	3598	3398	3573	2075	2.3
A-7	A66-36-60	115	7.10	3328		1.5	3370	3157	3342	1934	2.7
A-8	A66-29-Old 30	517	7.20	3360		1.2	3386	3185	3360	1960	1.6

	Core Identification	Station	Length	Weight As Received	Weight After 48 Hr. Soak	% Air	Weight After 2 Hr. Soak	Weight After Drying Period	Weight After 48 Hr. Soak	Weight In Water	% Air
B-1	A66-65-65	12	8.0					3328	3534	1962	7.5
B-2	A66-57-20	168	8.0					3166	3385	1863	7.6
B-3	A66-51-383	22	7.0					2770	2934	1695	2.5
B-4	A66-51-6	1923 & 75	8.1					3580	3782	2192	2.8
B-5	A66-50-14	765 & 80	7.9					3480	3672	2120	3.1
B-6	A66-41-14	37	7.4					3192	3355	1954	2.4
B-7	A66-36-60	115	7.5					3185	3370	1950	2.3
B-8	A66-29-Old 30	517	7.1					3090	3250	1897	1.9

	Core Identification	Station	Length	Weight As Received	Weight After 48 Hr. Soak	% Air	Weight After 2 Hr. Soak	Weight After Drying Period	Weight After 48 Hr. Soak	Weight In Water	% Air
C-1	A66-65-65	12	8.1					3340	3545	1967	7.6
C-2	A66-57-20	168	8.0					3214	3424	1913	6.3
C-3	A66-51-383	22	7.1					2993	3165	1833	2.7
C-4	A66-51-6	1923& 75	8.0					3507	3705	2141	2.9
C-5	A66-50-14	765 & 80	8.1					3481	3680	2124	3.0
C-6	A66-41-14	37	7.6					3284	3464	2039	1.6
C-7	A66-36-60	115	7.3					3050	3235	1870	2.4
C-8	A66-29-01d 30	517	7.0					2972	3124	1818	2.0